as in the following reference were made available to us by those authors by courtesy of the Oak Ridge National Laboratories. The Tl^{+*} states were calculated in a configuration which is the ground state with a $6s_{1/2}$ electron replaced by the state noted and the calculation carried to a new self-consistency. T. C. Tucker, L. D. Roberts, C. W. Nestor, Jr., T. A. Carlson, and F. B. Malik, Phys. Rev. 178, 998 (1969).

[16] J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, 215 (1962).

[17] The validity of the LCAO method depends a great deal on the smallness of the overlap of neighboring wave functions. In this work the largest value of overlap, 0.077, is for the Tl^+ $6s_{1/2}$-Br^- $4p_{3/2}$ nearest-neighbor wave functions (only considering valence basis). Maximum values reported for the LCAO calculations of KCl and AgCl are 0.07 (Ref. 12) and 0.078 (Ref. 13), respectively. The remaining smaller overlaps (including second nearest neighbors) of this work are also comparable to smaller values reported in Refs. 12 and 13.

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g and Hyperfine Components of V_K Centers*

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Experimental values of the g and hyperfine components of X_2^- V_K centers and Y_2^- V_K-type centers (X, Y = F, Cl, Br, I) in a large number of pure (AX) and doped ($AX:Y^-$) alkali halides have been determined through a careful analysis of their electron-paramagnetic-resonance (EPR) spectra. Expressions for the g components have been derived. For an accurate quantitative analysis, it is necessary to take into account the overlap terms in the calculation of δ, the matrix element of the orbital angular momentum $\vec{l}$ between the ${}^2\Sigma_u^+$ ground state and the ${}^2\Pi_u$ state. A calculation for Cl_2^- yields $\delta = 0.78$. Representative experimental values for Cl_2^- and Br_2^- are $\delta = 0.73$ and 0.70, respectively. The ${}^2\Sigma_u^+ - {}^2\Pi_u$ energy differences thus determined decrease going from the Rb salt to the Li salt. This behavior, in general, parallels that of the ${}^2\Sigma_u^+ - {}^2\Sigma_g^+$ and ${}^2\Sigma_u^+ - {}^2\Pi_g$ energy differences which are known from the optical-absorption measurements. The crystal field splitting of the ${}^2\Pi_u$ state is determined from the orthorhombic character of the g tensor. Expressions for the hyperfine components have been derived which include the first- and second-order correction terms originating from the combined effect of the spin-orbit and hyperfine operators. From the analysis of the combined behavior of the orthorhombic character of the g and hyperfine (hf) components, it can be concluded that $A_\parallel > 0$ and $A_\perp > 0$ for Cl_2^-, Br_2^-, and I_2^-, and $A_\parallel > 0$ and $A_\perp < 0$ for F_2^-. The analysis of the hf components then shows that the isotropic part of the hf interaction decreases monotonically going from the Rb to the Li salt, while the anisotropic part remains approximately constant. EPR results for V_{KA}, V_{KAA}, and V_F centers are also given and they are compared with the V_K-center data.

I. INTRODUCTION

The V_K center is the fundamental trapped-hole center in the alkali halides. Its geometric structure has been well established by electron-spin-resonance,[1] optical-absorption,[2,3] and electron-nuclear-double-resonance (ENDOR) measurements.[4] The hole is self-trapped by two neighboring substitutional X^- halogen ions as a $\langle 110 \rangle$-oriented X_2^- molecule ion occupying two negative-ion sites.[5]

The understanding of the properties of the V_K center is of fundamental importance. A large number of homonuclear and heteronuclear hole centers in the alkali halides (and other materials) are either derived from it or related to it[5] (e.g., the V_{KA} centers,[6,7] the V_F centers,[7-9] and the heteronuclear V_K-type hole centers[9,10]). Furthermore, the interstitial halogen-atom centers (i.e., the H center[11,12] and the centers derived from it[13-17]) are also X_2^- molecule ions but occupying only a single negative-ion site. Finally, the excitonic luminescence in alkali halides is described in terms of a relaxed (V_K + electron) system.[5,18,19]

The properties of the V_K center, especially those of the ground state, appear to be very close to those of the ${}^2\Sigma_u^+$ ground state of the free X_2^- halogen molecule ion. One expects that the differences between V_K and free X_2^- will become more pronounced in the excited states, because the lattice will affect V_K-center excited states more than the ground state and will tend to delocalize them. However, no direct comparison between V_K and free X_2^- is possible for the moment, because no relevant experimental spectroscopic data are available for the latter. At present the only source for comparison can be found in the elaborate self-consistent-field-molecular-orbital (SCF-MO) calculations of Gilbert and Wahl[20] on F_2^- and Cl_2^-. These wave functions were used by Jette, Gilbert, and Das[21] in their theory of the V_K center in alkali halides. These authors obtained some degree of quantitative agreement between the calculated and observed V_K-center quantities, primarily the optical transitions and the hyperfine interaction in the ground state. However, these calculations also made it clear that a more sophisticated and elaborate theory will be required. Similarly, more accurate and more systematic experimental data on the V_K centers are needed. Not only will they provide a stringent and systematic test for the theory, but hopefully some properties may be uncovered which will provide new insights into the electronic structure of the V_K center.

In this paper extensive and accurate electron-paramagnetic-resonance (EPR) data on the V_K and V_K-type centers will be presented. The production of the centers and the analysis of the EPR spectra is given in Secs. III and IV. Sections V and VI then present a simple but careful analysis of the g components—which have received little detailed attention up to now—and the hyperfine components. Finally, in Sec. VII, EPR and optical-absorption results for some V_{KA}, V_{KAA}, and V_F centers are presented briefly because they permit interesting comparisons with the V_K-center data.

II. EXPERIMENTAL

The crystals used in these experiments were grown in air by the Kyropoulos method. The alkali fluorides were grown from melts of reagent-grade material to which nothing else was added. The chlorides and bromides were grown from melts to which in general one of the following impurities was added: Pb^{++}, Ag^+, Tl^+, and NO_2^- or NO_3^-. These impurities act as very good electron traps in these two types of alkali halides.[2,3] The heavy-metal ions are incorporated in the lattice by adding to the melt up to about 1 wt% of the corresponding halogen salt. The NO_2^- and NO_3^- are incorporated by adding to the melt up to about 0.5 wt% of the corresponding alkali nitrate or nitrite. Also grown were (a) alkali chlorides (with electron traps) to which had been added in the melt about 1 wt% of the corresponding alkali bromide or alkali iodide and (b) alkali bromides to which were added about 1 wt% of the corresponding alkali iodide. Not all of the possible combinations of the aforementioned alkali halides and electron traps were grown. In general, Pb^{++} was preferred. The NO_2^- or NO_3^- ions were the next preferred choice. The alkali iodides were grown only with Tl^+ or NO_2^- impurities.

The centers were produced by exposure either to x rays from a Machlett tube (60 kV, 40 mA), or to γ rays from an 18-kCi ^{60}Co source. The length of the irradiation was several minutes for crystals which contained an electron trap. Details of the EPR measurements have been given before.[9,10] The g factors were determined with respect to $g = 2.0036$ of diphenylpicrylhydrazyl (DPPH), a little speck of which was positioned immediately next to the crystal in the microwave cavity.

III. PRODUCTION OF V_K AND V_K-TYPE CENTERS

The production of the X_2^- V_K centers in the AX alkali halides is straightforward. They are produced by irradiating the crystal with x or γ rays at sufficiently low temperatures. These ionizing radiations produce, among other things, electrons and holes. In the pure undoped alkali halide, the electrons are mainly trapped by negative-ion vacancies as F and F' centers, while the holes are self-trapped by two neighboring substitutional X^- ions as $\langle 110\rangle$-oriented X_2^- molecule ions, i.e., as V_K centers. The rate of production and the concentration of V_K centers is enhanced substantially in the alkali chlorides, bromides, and iodides, if they contain one of the following electron traps: Pb^{++}, Tl^+, Ag^+, and NO_2^- or NO_3^- ions. These ions trap electrons and become Pb^+, Tl^0, Ag^0, NO_2^{--}, or NO_3^{--}. These species have been studied by optical-absorption and/or EPR techniques.[22-25] The F_2^- V_K center in the alkali fluorides is readily produced in the nondoped crystals grown from reagent-grade starting material, and it is suspected that an unintentional impurity (possibly Mg^{++}) acts as an electron trap.

Practically all X_2^- V_K centers are stable at 77 K and they can be produced by x or γ irradiation at this temperature. A known exception is the I_2^- V_K center in NaI.[26] It appears also likely that the V_K centers in LiBr and LiI—if indeed they can be produced in these materials—are not stable at 77 K. These two crystals were not investigated, however, because of their high hygroscopic character.

The V_K centers are stable at 77 K, but decay at sufficiently high temperatures. The decay temperature T_{decay} depends on the center and on the crystal. Tables I–IV give the T_{decay} of the V_K centers as determined by the pulse-anneal technique. It is a consequence of the V_K-center structure that the diffusion mechanism (which results in the eventual decay of the center) is identical to the thermal-reorientation (or -disorientation) mechanism. The latter is responsible for the thermal decay of the optical anisotropy which can be produced by an intense beam of polarized light in the optical-absorption bands of the V_K center.[2,3,26,27] The reorientation frequency is about 0.01 Hz around the disorientation temperature T_{dis} and $\sim 10^3$ Hz around the decay temperature T_{decay}. If it is assumed that the frequency factor of this process is about the same for all V_K centers, the disorientation temperatures given in Tables I–IV are proportional to the activation energies. From the knowledge that, e.g., $E = 0.51$ eV for Cl_2^- in

TABLE I. Spin-Hamiltonian parameters at 77 K and some thermal data of the F_2^- V_K centers in the alkali fluorides. The hyperfine parameters and the linewidth ΔH (between the extrema of the first derivative) are expressed in G. The decay temperature T_{decay} and the disorientation temperature T_{dis} are given in °K.

Crystal	g_z [110]	g_x [001]	g_y [110]	A_z [110]	$A_\perp = \frac{1}{2}(A_x + A_y)$	ΔH	T_{decay} T_{dis}
RbF [a]	2.003 ± 0.002	(2.0160)		+908.4 ± 0.3	···	11 ± 1	··· ···
KF	2.0020 ± 0.0003	2.0227 ± 0.0002	2.0208 ± 0.0002	+908.1 ± 0.3	−28 ± 2	2.3 ± 0.1	210 ···
NaF	2.0017 ± 0.0003	2.0232 ± 0.0003	2.0226 ± 0.0003	+898.1 ± 0.5	−47 ± 4	9.0 ± 0.5	160 140[b]
LiF	2.003 ± 0.001	2.0234 ± 0.0003	2.0227 ± 0.0003	+887 ± 0.5	−58 ± 4	12.9 ± 0.5	125 113[c]

[a] From Ref. 31. [b] D. Schoemaker (unpublished results). [c] From Ref. 3.

KCl,[27] one can obtain by a simple scaling procedure, the approximate activation energies for reorientation of the V_K centers.

At the decay temperature, the X_2^- center, or the hole for that matter, moves rapidly through the lattice. Several things may happen. The hole may encounter a trapped electron center such as Pb^+, Tl^0, Ag^0 and these species are restored to Pb^{++}, Tl^+, Ag^+. However, the probability of this process is rather small since for the doping levels that are used, only a small fraction of the Pb^{++}, Tl^+, or Ag^+ ions is used up as electron traps. Therefore, the probability that the hole encounters Pb^{++}, Tl^+, or Ag^+ is much higher, and it is observed that these ions can also trap the mobile hole. As a result, Pb^{+++}, Tl^{++}, or Ag^{++} is formed, and these species have been studied by optical-absorption and EPR techniques.[22,28,29] If the AX alkali halide contains, furthermore, a small amount of a foreign Y^- halogen ion, whose electronegativity is smaller than the electronegativity of X^-, then the hole may also be retrapped and a ⟨110⟩-oriented heteronuclear XY^- V_K-type center is formed. Examples are $BrCl^-$ in KCl : Br^-,[10] ICl^- in KCl : I^-,[30] and IBr^- in KBr : I^-.[9,10] If the concentration of Y^- is sufficiently high (~ 1 wt%), there is a reasonable probability that two Y^- impurity ions occupy nearest-neighbor positions. These pairs of Y^-, it is observed, can also trap the mobile hole, and consequently ⟨110⟩-oriented Y_2^- V_K-type centers are produced in the AX lattice. The Y_2^- concentration is increased further when the XY^- centers decay. The production of V_K-type I_2^- centers in KCl : I^- and KBr : I^- has been discussed before,[9] and the production of Br_2^- in the Br^--doped alkali chlorides is completely analogous.

No systematic study of the decay temperatures of the Y_2^- centers in the AX lattice has been performed. The observed decay temperature depends very often on the nature of the added electron trap. For instance, in KCl : (Br^-, Pb^{++}) the Br_2^- V_K-type center decays at about − 50 °C. This is not the "true" decay temperature of this Br_2^- center in the sense that the positive hole breaks away and leaves behind two substitutional Br^- ions. Rather, a positive-ion vacancy (introduced in the lattice by the divalent Pb^{++}) moves over to Br_2^-, and as a result a V_F-type Br_2^- is formed.[7] This process at − 50 °C has

TABLE II. Spin-Hamiltonian parameters at 77 K and some thermal data of the $^{35}Cl_2^-$ V_K centers in the alkali chlorides.

Crystal	g_z [110]	g_x [001]	g_y [$1\bar{1}0$]	A_z [110]	$A_\perp$ $=\frac{1}{2}(A_x + A_y)$	$\Delta A_\perp$ $=\frac{1}{2}(A_x + A_y)$	P	ΔH	δ (expt.)	T_{decay} T_{dis}[a]
RbCl	2.00150 ± 0.00010	2.0460 ± 0.0002	2.0399 ± 0.0002	+101.92 ± 0.05	+12.55	+0.17	(−4.87)[b]	9.0 ± 0.5	0.75	220 188
KCl	2.00145 ± 0.00005	2.0445 ± 0.0001	2.0424 ± 0.0001	+101.31 ± 0.05	+12.13	+0.14	−4.87 ± 0.05	1.4 ± 0.1	0.73	210 173
NaCl	2.00132 ± 0.00010	2.0424 ± 0.0002	2.0492 ± 0.0002	+98.71 ± 0.05	+9.04	−0.14	(−4.87)[b]	5.6 ± 0.5	0.72	150 133
LiCl	2.00140 ± 0.00010	2.0432 ± 0.0002	2.0569 ± 0.0002	+95.54 ± 0.05	+6.23	−0.56	(−4.87)[b]	5.6 ± 0.5	0.82	120 103

[a] From Ref. 10. [b] Value used in the analysis.

TABLE III. Spin-Hamiltonian parameters at 77 K and some thermal data of the $^{81}Br_2^-$ V_K centers in the alkali bromides, and the V_K-type $^{81}Br_2^-$ centers in Br^--doped alkali chlorides.

Crystal	g_z [110]	g_x [001]	g_y $[1\bar{1}0]$	A_z [110]	$A_\perp = \frac{1}{2}(A_x+A_y)$	$\Delta A_\perp = \frac{1}{2}(A_x-A_y)$	P	ΔH	δ (expt.)	T_{decay} T_{dis}
RbBr	1.9846	2.1683	2.1524	+454.9	+82.4	+1.2	+28.7	10.5	0.700	170
	± 0.0001	± 0.0003	± 0.0002	± 0.1	± 0.3		± 0.2			...
KBr	1.9839	2.1629	2.1623	+450.2	+76.7	+0.1	+28.4	3.8	0.699	160
	± 0.0001	± 0.0002	± 0.0001	± 0.1	± 0.3		± 0.2			143[b]
NaBr	1.9791	2.1514	2.1968	+431.0	+69.4	−4.4	+28.5	12	0.686	115
	± 0.0001	± 0.0005	± 0.0004	± 0.1	± 0.7		± 0.2			...
RbCl : Br⁻	1.9838	2.1752	2.1518	+454.6	+85.7	+2.0	+28.4	14	0.701	> 300[a]
	± 0.0001	± 0.0004	± 0.0003	± 0.1	± 0.3		± 0.2			
KCl : Br⁻	1.9830	2.1692	2.1637	+450.5	+81.0	+0.7	+28.6	2.8	0.702	>300[a]
	± 0.0001	± 0.0001	± 0.0001	± 0.1	± 0.2		± 0.2			
NaCl : Br⁻	1.9787	2.1549	2.1938	+434.4	+71.5	−3.8	+29.0	7	0.683	>300[a]
	± 0.0001	± 0.0004	± 0.0003	± 0.1	± 0.5		± 0.2			
LiCl : Br⁻	1.9751	2.1416	2.2104	+420.1	+64.8	−5.3	+27.6	10	0.656	> 300[a]
	± 0.0001	± 0.0006	± 0.0005	± 0.1	± 0.9		± 0.2			

[a] In the NO_2^--NO_3^-–doped crystals (see text).

[b] From Ref. 3.

been described in more detail for the I_2^- V_K- and V_F-type centers in the KCl : (I^-, Pb^{++}) system.[9] In KCl : (Br^-, Tl^+), on the other hand, a large fraction of the Br_2^- disappears around 0 °C. Again this is not the true Br_2^- decay temperature: It decays because the Tl^0 loses its electron at 0 °C.[23] In KCl : (Br^-, NO_2^-) finally, the Br_2^- V_K-type center decays at about + 50 °C. This could very well represent the true Br_2^- decay temperature, but no detailed studies were performed in this and other crystals to confirm this. However, it was verified that all the V_K-type Br_2^- centers in the Br^--doped alkali chlorides are quite stable at room temperature (at least for $\frac{1}{2}$ h or so) in the nitrate-nitrite-doped crystals.

The existence of V_K-type Br_2^- in the alkali-chloride lattice makes it possible to produce an isotopically pure Br_2^- EPR spectrum. By doping *very pure* KCl (Br^- is a common impurity!) with, e.g., the enriched $^{79}Br^-$ isotope, one can produce exclusively $^{79}Br\,^{79}Br^-$ centers. The complete unravelling of the EPR spectrum, especially with regard to the "forbidden" transitions, would be much easier in this case.

Finally, it might be mentioned that the concept of reorientation has of course no meaning for a Y_2^- center in an AX lattice.

IV. EPR SPECTRA

The identification of the structure and symmetry of the V_K and V_K-type centers through their well-resolved EPR spectra has been described thoroughly in the literature[1,9,31] and will not be repeated here. The unpaired electron spin of the X_2^- molecule ion interacts with the two equivalent X nuclei, and the spin Hamiltonian, to which the carefully measured EPR spectra were matched, was taken as

$$\frac{\mathcal{H}}{g_0\mu_B} = \frac{1}{g_0}\left(g_zH_zS_z + g_xH_xS_x + g_yH_yS_y\right) + \sum_{i=1}^{2}\left(A_zS_zI_{z,i} + A_xS_xI_{x,i} + A_yS_yI_{y,i}\right)$$

TABLE IV. Spin-Hamiltonian parameters of the I_2^- V_K centers at 77 K in RbI and KI and at 40 K in NaI.

Crystal	$A_\parallel$ [110]	$A_\perp = \frac{1}{2}(A_x+A_y)$	g_z [110]	g_x [001]	g_y $[1\bar{1}0]$	P	ΔH	T_{decay} T_{dis}
RbI[a]	+394.4	+141	1.9121	(2.35)[b]	2.210	+32.2	13.3	125[c]
	± 0.1	± 5	± 0.0005		± 0.021	± 0.5	± 0.5	100[c]
KI[d]	+384.8	+140	1.9037	(2.29)[b]	2.266	+33.2	11.0	105
	± 0.1	± 5	± 0.0005		± 0.021	±0.5[e]	± 0.5	93[e]
NaI[a]	+344.2	+140	1.8584	(2.27)[d]	2.340	+29.5	33	58[c]
	± 0.2	± 10	± 0.0011		± 0.037	± 2	± 0.5	50[c]

[a] From Ref. 32.

[b] Estimated (this paper).

[c] From Ref. 26.

[d] From Ref. 9; in this paper, the results for the V_K- and V_F-type I_2^- in KCl : KI and KBr : KI can also be found.

[e] From Ref. 3.

$$+P\sum_{i=1}^{2} I_{z,i}^{2} - \frac{g_N \mu_N}{g_0 \mu_B}\vec{\mathrm{H}}\cdot\sum_{i=1}^{2}\vec{\mathrm{I}}_i \quad . \quad (1)$$

The symbols have their usual meaning and the axes are defined as the molecular axis $z \parallel [110]$, $y \parallel [1\bar{1}0]$, and $x \parallel [001]$.

The F_2^- spectra ($\theta = 0°$, $35.26°$, $60°$, and $90°$, in which θ is the angle between $\vec{\mathrm{H}}$ and z) were analyzed with a perturbation solution[9] of (1). The results in Table I are in good agreement with those obtained earlier by Bailey[31] and Castner, Känzig, and Woodruff.[1] For the I_2^- center in KI only the $\theta = 0°$ spectrum ($\vec{\mathrm{H}} \parallel \langle 110 \rangle$) was analyzed. Again a perturbation solution of (1) was used. The analysis of the $\theta \neq 0°$ spectra, which permits the determination of $g_\perp$, and the analysis of I_2^- in NaI and RbI was performed by Repka,[32] and these results have been included in Table IV. It should be noted that the $g_\perp$ value determined by Repka is actually g_y because his analysis was limited to an angular-variation study in a $\{100\}$ plane.

The Cl_2^- and Br_2^- spectra too were originally treated with the second-order perturbation solution of (1), and the following spectra were analyzed: (i) the $\theta = 0°$ spectrum observable when $\vec{\mathrm{H}} \parallel \langle 110 \rangle$; (ii) the triply degenerate $\theta = 35.26°$, $\varphi = 90°$ spectrum observable when $\vec{\mathrm{H}} \parallel \langle 111 \rangle$; (iii) the $\theta = 35.26°$ $\varphi = 0°$ spectrum observable when the magnetic field $\vec{\mathrm{H}}$ makes a $35.26°$ angle with $\langle 110 \rangle$ in a $\{001\}$ plane. Extrapolation of the g values of the latter two spectra to $\theta = 90°$ yields, respectively, g_x and g_y. The quadrupole parameters P of Cl_2^- in KCl and of all the Br_2^- centers were determined from the analysis of the weakly allowed ΔM_1 or $\Delta M_2 = \pm 1$ transitions. These are readily observed and identified in the $\theta = 45°$ spectrum ($\vec{\mathrm{H}} \parallel \langle 100 \rangle$) for Cl_2^- in KCl, and in the $\theta = 35.26°$ ($\vec{\mathrm{H}} \parallel \langle 111 \rangle$), $\theta = 45°$ ($\vec{\mathrm{H}} \parallel \langle 100 \rangle$), and $\theta = 60°$ ($\vec{\mathrm{H}} \parallel \langle 110 \rangle$) spectra for Br_2^-. In the later stages of the analysis, a computer program, involving a matrix diagonalization of (1) and a least-squares-fitting routine, was used. All the Cl_2^- and Br_2^- centers were carefully reanalyzed with this computer program, and a very good over-all fit was obtained. It was gratifying to see that the results obtained by the perturbation solution were very close to the computer results. The computer analysis made it also possible to determine the orthorhombic character of the hyperfine (hf) tensor. The results are given in Tables II and III. A special effort was made to determine the $g_\parallel$ factors of the Cl_2^- centers as accurately as possible, though we did not achieve in all cases the desired accuracy ($\sim \pm 0.00005$). The $g_\parallel$ value of Cl_2^- in KCl is the average of a very large number of measurements on different samples. The parameters given in Tables I–IV are believed to be the most accurate to date, and the quoted errors are in general on the conservative side. In Secs. V–VIII a simple but careful analysis of the EPR data will be presented.

V. g COMPONENTS

An analysis of the excited $^2\Pi_g$ state of the neutral X_2 molecules,[33] and SCF calculations for F_2^- and Cl_2^- molecules,[20] show that the X_2^- molecule ions are stable with binding energies ranging from ~ 0.7 eV for I_2^- to ~ 1.5 eV for F_2^-, and the ground-state configuration of the valence electrons is

$$\ldots (\sigma_g)^2 (\pi_u)^4 (\pi_g)^4 (\sigma_u)^1 \ , \quad {}^2\Sigma_u^+ \ . \qquad (2)$$

The excited states arising from the $\pi_u \rightarrow \sigma_u$ and $\pi_g \rightarrow \sigma_u$ excitations are $^2\Pi_{u(1/2,3/2)}$ and $^2\Pi_{g(1/2,3/2)}$, and the spin-orbit interaction lifts the degeneracy between the $J_z = \frac{1}{2}$ and $J_z = \frac{3}{2}$ components.

The relatively large binding energy is the basic reason why holes in alkali halides (and in many other materials containing halogen ions) are self-trapped as X_2^- molecule ions. (A known exception is AgCl where the hole is self-trapped as Ag^{++}[34,35].) In doing so, the hole becomes deeply trapped in the crystal and the experimental EPR spectra show that the ground state of the V_K center is a very well-localized state. The same is true for the Y_2^- V_K-type centers in $AX : Y^-$, but, stabilization of the hole in this case is helped by the fact that the electronegativity of Y^- is lower than the electronegativity of X^-. The EPR spectra show no resolved hyperfine interaction with nuclei other than the two X nuclei, and the linewidths, which are quite narrow, can be explained for the greater part by simple dipole-dipole interaction between the unpaired electron and the surrounding nuclei.[36] Furthermore, optical-absorption measurements on the V_K centers[2,3,26] yield two well-defined absorption bands whose position and polarization properties are such that they can be associated in a straightforward manner with the $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ and $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transitions of the free molecule ion. In fact, for the F_2^- and Cl_2^- centers there is reasonable quantitative agreement between the experimental and calculated absorption bands.[21] This seems to indicate that also the excited states of the V_K center are reasonably well-localized states and that (2) is a good starting point for a description of the various experimental results. One can look upon (2) as a set of discrete localized orbitals which have been split off the valence band by the self-trapping process.[37]

In the case of the V_K center in alkali halides of NaCl structure, the symmetry of the X_2^- molecule ion and surroundings is D_{2h}, and the orbitals in (2) can be classified accordingly. The x and y components of π_u are split into b_{3u} and b_{2u}, and into b_{2g} and b_{3g} for π_g.[38] The configuration scheme of the valence orbitals of the V_K center can be written

$$\ldots (a_g)^2 (b_{3u})^2 (b_{2u})^2 (b_{2g})^2 (b_{3g})^2 (b_{1u}) \ , \quad {}^2B_{1u} \ . \qquad (3)$$

There are two ways of looking at (3). In the case where both the ground and excited states are very well localized, b_{3u} and b_{2u}, e.g., are the two components of π_u whose degeneracy is lifted, and whose shape is distorted, by the electrostatic field of the polarized lattice surrounding the X_2^- molecule ion. The separation and the relative position of b_{3u} and b_{2u} depend then on the strength and the sign of the electrostatic field. In the case where the excited states are not so well localized, b_{3u} and b_{2u} must be considered as molecular orbitals which are not wholly confined around the two X nuclei, but extend to some degree over the surrounding ions of the lattice. The separation and position of b_{3u} and b_{2u} is then determined by the relative energies of the extended and suitably orthogonalized b_{3u} and b_{2u} molecular orbitals in the lattice. At least in some cases this last viewpoint may eventually prove to be a more fruitful one for accurate quantitative treatments. As long as delocalization of the excited states is small, (3) provides a good basis for discussing the various properties of the V_K center. However, if delocalization of the excited states should be appreciable, (3) would be only an approximation, since other states would be split off the valence band. These states could also contribute to the g shifts and give rise to other optical-absorption bands than the two already observed.

There seems to be no compelling reason so far to go beyond the approximation implied by (3), and so the calculation of the g components will be based on it. Small delocalization effects can be absorbed in some of the parameters that occur in the expressions of the g components. For convenience we will use the concept of a crystalline field as a vehicle for discussing the lifting of the degeneracy of the $^2\Pi$ states of the X_2^- molecule ion, but the limitations of this concept should be kept in mind.

From the fact that the g tensors do not deviate very much from axial symmetry, one deduces that the separation of the excited $^2B_{2u}$ and $^2B_{3u}$ states caused by the crystal field is quite small, of the order of a few tenths of an eV. (From the study of the $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ optical transitions,[2,3] one can deduce that the same is true for the excited $^2B_{2g}$ and $^2B_{3g}$ states.) This splitting is oftentimes comparable to the spin-orbit splitting, and both interactions should be treated on an equal basis in discussing the separation of $^2B_{2u}$ and $^2B_{3u}$.

The spin-orbit operator of an electron moving in the electrostatic field $\vec{E} = \vec{\nabla} V$ of the molecule is[39,40]

$$\mathcal{H}_{so} = \frac{e\hbar^2}{2m^2c^2}\,\vec{s}\cdot(\vec{E}\times\vec{p}) = \mathfrak{L}_x s_x + \mathfrak{L}_y s_y + \mathfrak{L}_z s_z\ ,$$

in which $\vec{p} = -i\vec{\nabla}$ is the momentum operator, e and m the charge and mass of the electron, c the velocity of light, and $\hbar = h/2\pi$. $\mathfrak{L}_x$, $\mathfrak{L}_y$, and $\mathfrak{L}_z$ transform, respectively, as b_{3g}, b_{2g}, and b_{1g}, and therefore only $\mathfrak{L}_z$ is nonzero between $|b_{2u}\rangle$ and $|b_{3u}\rangle$.[38]

The two 2×2 matrices of the spin-orbit operator $\mathcal{H}_{so}$ and the crystalline-field operator $\mathcal{H}_V$, spanned by $|b_{3u}+\rangle$, $|b_{2u}+\rangle$, $|b_{3u}-\rangle$, and $|b_{2u}-\rangle$, are easily solved. $\mathcal{H}_V$ is diagonal in $|b_{2u}\rangle$ and $|b_{3u}\rangle$ and defining a spin-orbit coupling constant

$$\lambda'_{1u} = -i\langle b_{3u}\pm|\mathfrak{L}_z|b_{2u}\pm\rangle\ , \tag{4}$$

the functions that diagonalize $\mathcal{H}_{so}$ and $\mathcal{H}_V$ simultaneously are found to be

$$\begin{aligned} |\pi_{2u}\pm\rangle &= a_u|b_{3u}\pm\rangle \pm ib_u|b_{2u}\pm\rangle\ ,\\ |\pi_{1u}\pm\rangle &= b_u|b_{3u}\pm\rangle \mp ia_u|b_{2u}\pm\rangle\ , \end{aligned} \tag{5}$$

with

$$a_u = k_u\lambda'_{1u}\ ,\qquad b_u = k_u[\Delta_u + (\Delta_u^2 + \lambda'^2_{1u})^{1/2}]\ , \tag{6}$$

in which k_u is the normalization constant and

$$\Delta_u = \langle b_{3u}|\mathcal{H}_V|b_{3u}\rangle - \langle b_{2u}|\mathcal{H}_V|b_{2u}\rangle \tag{7}$$

is the crystal-field-splitting parameter. Expressions (5) and (6) have been written so that $a_u > 0$. In the absence of a crystalline field ($\Delta_u = 0$), $a_u = b_u = 1/\sqrt{2}$ and the $|\pi_{2u}\pm\rangle$ define $^2\Pi_{u\,3/2}$, and $|\pi_{1u}\pm\rangle$ define $^2\Pi_{u\,1/2}$. If E_{2u} and E_{1u} are the energies of the $\pi_{2u} \rightarrow b_{1u}$ and $\pi_{1u} \rightarrow b_{1u}$ excitations, one finds, to this order of approximation, that their separation is given by

$$E_{2u} - E_{1u} = (\Delta_u^2 + \lambda'^2_{1u})^{1/2}\ .$$

However, the spin-orbit interaction is not diagonal in representation (2) and $|a_u\rangle$ is mixed into $|b_{2u}\rangle$ and $|b_{3u}\rangle$. This contributes to the splitting of b_{2u} and b_{3u} and one finds

$$E_{2u} - E_{1u} = (\Delta_u^2 + \lambda'^2_{1u})^{1/2} + a_u b_u \lambda_{1u}^2/E_{\perp u}\ , \tag{8}$$

in which $E_{\perp u}$ is an average of E_{2u} and E_{1u}, and λ_{1u} is defined in (12) later on.

Digressing here for a moment, we note that the foregoing calculation can be repeated almost exactly for the excited $^2\Pi_g$ states which are involved in the $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ optical transitions. One finds that the splitting of the $^2\Pi_g$ states is given by (see Fig. 1)

$$E_{2g} - E_{1g} = (\Delta_g^2 + \lambda'^2_{1g})^{1/2} - \frac{a_g b_g \lambda_{1g}^2}{E_\sigma - E_{\perp g}} \tag{9}$$

in which the g quantities are defined exactly as the u quantities in (8).

We can now proceed with the calculation of the g components. The ground state $^2B_{1u}(^2\Sigma_u^+)$ is an orbital singlet, and in the absence of spin-orbit interaction the Zeeman splitting of the two-electron spin states would be determined by the free-electron g factor $g_0 = 2.00229$. However, spin-orbit interaction mixes the $^2B_{2u}$ and $^2B_{3u}$ states into $^2B_{1u}$

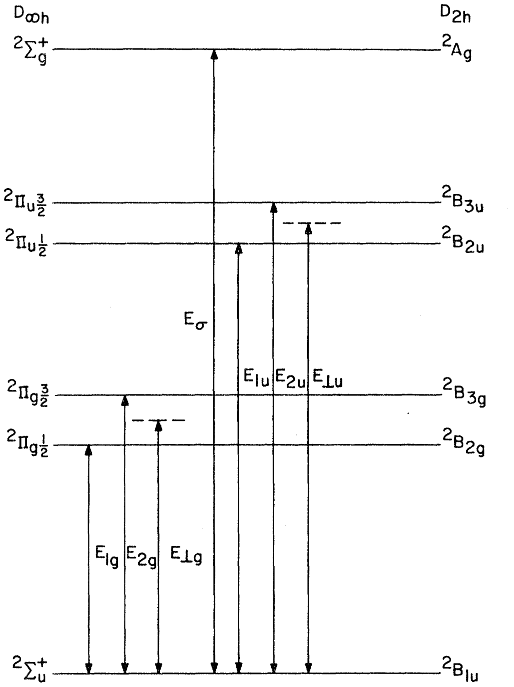

FIG. 1. Schematic energy-level scheme of the V_K center.

and as a result the orbital angular momentum contributes to the Zeeman splitting, resulting in an anisotropic g factor different from g_0.

The Zeeman operator is

$$\mathcal{H}_Z = \mu_B \vec{H} \cdot (\vec{l} + g_0 \vec{s}) , \tag{10}$$

where the orbital angular-momentum operator $\vec{l} = \vec{r} \times \vec{p}$ can be referred to an arbitrary set of axes. The combined effect of $\mathcal{H}_{so}$ and $\mathcal{H}_Z$ on the spin degeneracy of $^2B_{1u}$ can be calculated with perturbation theory. The matrix elements which are zero are again easily determined by symmetry arguments[38] by noting that l_x, l_y, and l_z in (10) transform, respectively, as b_{3g}, b_{2g}, and b_{1g}. It is found that only $|b_{3u}\pm\rangle$ and $|b_{2u}\pm\rangle$, i.e., the combinations $|\pi_{1u}\pm\rangle$ and $|\pi_{2u}\pm\rangle$, contribute to the calculation. Using third-order perturbation theory, one calculates to second order in λ/E,

$$\begin{aligned}
\Delta g_z &= g_z - g_0 = -\left[\frac{g_0}{2}\left(\frac{1}{E_{1u}^2} + \frac{1}{E_{2u}^2}\right) - \frac{\delta_z}{E_{1u}E_{2u}}\right]\lambda_{1u}^2 , \\
\Delta g_x &= g_x - g_0 = \frac{2b_u^2\delta_y\lambda_{1u,y}}{E_{1u}} + \frac{2a_u^2\delta_x\lambda_{1u,x}}{E_{2u}} \\
&\qquad - \frac{g_0}{2}\lambda_{1u}^2\left(\frac{a_u^2}{E_{2u}^2} + \frac{b_u^2}{E_{1u}^2}\right) - \frac{\lambda_{1u}\lambda'_{1u}\delta}{E_{1u}E_{2u}} , \\
\Delta g_y &= g_y - g_0 = \frac{2a_u^2\delta_y\lambda_{1u,y}}{E_{1u}} + \frac{2b_u^2\delta_x\lambda_{1u,x}}{E_{2u}} \\
&\qquad - \frac{g_0}{2}\lambda_{1u}^2\left(\frac{b_u^2}{E_{2u}^2} + \frac{a_u^2}{E_{1u}^2}\right) - \frac{\lambda_{1u}\lambda'_{1u}\delta}{E_{1u}E_{2u}} ,
\end{aligned} \tag{11}$$

in which

$$\begin{aligned}
\lambda_{1u,x} &= -i\langle b_{1u}|\mathcal{L}_x|b_{2u}\rangle , \\
\lambda_{1u,y} &= -i\langle b_{1u}|\mathcal{L}_y|b_{3u}\rangle , \\
\delta_x &= -i\langle b_{1u}|l_x|b_{2u}\rangle , \\
\delta_y &= -i\langle b_{1u}|l_y|b_{3u}\rangle , \\
\delta_z &= -i\langle b_{3u}|l_z|b_{2u}\rangle .
\end{aligned} \tag{12}$$

For simplicity we have made the following approximations in the second-order terms: $\delta \approx \delta_x \approx \delta_y$ and $\lambda_{1u} = \lambda_{1u,x} = \lambda_{1u,y}$. For the V_K centers, deviations from axial symmetry are in general small, and this approximation is not a serious one. Note that apart from this, the structure of (11) is independent of any approximation for the molecular orbitals and the operators $\mathcal{H}_{so}$ and $\mathcal{H}_Z$. Formulas (11) have been written such that λ_{1u} and δ must be taken as positive. Consequently, Δg_x and Δg_y are predominantly first order and positive, while Δg_z is completely second order and negative. These results, which are in agreement with experiment, have been obtained before by a less-general calculation.[41] For a numerical analysis we must make some approximations for the orbitals and the operators. For the orbitals we restrict ourselves to the free molecule ion (for which immediately $\delta_z = 1$) and we take the following simple linear combination of atomic orbitals (LCAO's):

$$\begin{aligned}
|b_{1u}\rangle &= \alpha_u(ns_1 - ns_2) + \beta_u(np_{z1} + np_{z2}) , \\
|b_{2g}\rangle &= \mu_g(np_{x1} - np_{x2}) , \\
|b_{3g}\rangle &= \mu_g(np_{y1} - np_{y2}) , \\
|b_{3u}\rangle &= \mu_u(np_{x1} + np_{x2}) , \\
|b_{2u}\rangle &= \mu_u(np_{y1} + np_{y2}) , \\
|a_g\rangle &= \alpha_g(ns_1 + ns_2) + \beta_g(np_{z1} - np_{z2}) ,
\end{aligned} \tag{13}$$

in which ns and $np_{x,y,z}$ are atomic s and p functions of the valence electrons of, what should preferably be, an $X^{-1/2}$ ion. With approximation (13) one has immediately $\delta_x = \delta_y = \delta$ and $\lambda_{1u,x} = \lambda_{1u,y} = \lambda_{1u}$, and this eliminates one possible source of the orthorhombic character of the g components. Since the spatial part of the spin-orbit operator decreases as r^{-3} with respect to each nucleus, overlap contributions to the spin-orbit coupling are small. Furthermore, since (3) or (2) is built up primarily from X and X^- valence electrons, it is a reasonable approximation for $\mathcal{H}_{so}$ to write

$$\mathcal{H}_{so} = \lambda \sum_{k=1}^{2} \vec{l}_k \cdot \vec{s} , \tag{14}$$

in which $\lambda > 0$ is the spin-orbit coupling constant for an np valence electron of the $X^{-1/2}$ ion, and $\vec{l}_k$ the

TABLE V. Atomic parameters of the $X^{-1/2}$ halogen ions. $\langle r^{-3}\rangle_{\mathrm{HF}}$ and $|\psi_{ns}(0)|^2$ are given in units of 10^{24} cm^{-3} and λ in cm^{-1} units.

	$\mathrm{F}^{-1/2}$	$\mathrm{Cl}^{-1/2}$	$\mathrm{Br}^{-1/2}$	$\mathrm{I}^{-1/2}$
λ	246	536	2259	4710
$\langle r^{-3}\rangle_{\mathrm{HF}}$	46.5	41.7	74.5	93.3
$\lvert\psi_{ns}(0)\rvert^2$	75.2	69.9	127.6	150.0

orbital-angular-momentum operator referred to nucleus k. The values of λ are given in Table V. They represent the average of the λ of the X^- ion and X^0 atom. These λ and the other atomic parameters of Table V were compiled from various sources. In evaluating λ_{1u} and λ'_{1u} from (4) and (12) using (14), the overlap effects amount only to a few percent, and will be neglected. Specifically,

$$\lambda_{1u} = 2\beta_u\mu_u\lambda \ , \quad \lambda'_{1u} = 2\mu_u^2\lambda \ . \tag{15}$$

If overlap is systematically neglected, l_x and l_y in (12) can be approximated by[39] $\sum_{k=1}^{2} l_{xk}$ and $\sum_{k=1}^{2} l_{yk}$. Calculation of δ then yields

$$\delta = 2\beta_u\mu_u \approx 1.07 \tag{16}$$

using the values of β_u and μ_u given later in (18). However, overlap effects have to be included in the calculation of δ since they produce sizable corrections. This calculation proceeds as follows.[42] The orbital angular momentum $\vec{l}$ in (10) can be referred to any set of axes. We refer it to a gauge with nucleus 1 as the origin, i.e.,

$$\vec{l} \equiv \vec{l}_1 = \vec{r}_1 \times \vec{p} \ ,$$

where $\vec{r}_1$ is the position vector of the unpaired hole with respect to nucleus 1, and $\vec{p}$ its momentum. $\vec{l}_1$ can be rewritten

$$\vec{l}_1 = (\vec{R} + \vec{r}_2) \times \vec{p} = \vec{R} \times \vec{p} + \vec{l}_2 \ ,$$

where $\vec{R}$ is the internuclear vector, directed from nucleus 1 to nucleus 2, and $\vec{r}_2$ the position vector of the unpaired electron with respect to nucleus 2. From here on the calculation of δ is straightforward and one finds

$$\delta = \delta_x = \delta_y = 2\beta_u\mu_u\left[1 + \tfrac{1}{2}(S_{\sigma\sigma} + S_{\pi\pi}) - \frac{1}{2}\frac{\alpha_u}{\beta_u}\left(R\,\langle s\,|\frac{\partial}{\partial y}\,|\,y\rangle + S_{\sigma s}\right)\right] \ , \tag{17}$$

in which

$$S_{\sigma\sigma} = \langle z_1 | z_2 \rangle = \langle z_1 | l_{y2} | x_2 \rangle < 0 \ ,$$
$$S_{\pi\pi} = \langle x_1 | x_2 \rangle = \langle x_1 | l_{y2} | z_2 \rangle > 0 \ ,$$
$$S_{\sigma s} = \langle z_1 | s_2 \rangle > 0$$

are overlap integrals, and $\langle s\,|\,\partial/\partial y\,|\,y\rangle = \langle s\,|\,\partial/\partial x\,|\,x\rangle$ is an atomic integral which was evaluated by Misetich and Watson.[43] There is not much variation of this integral throughout the halogens or going from the halogen atom to the halogen negative ion. For our pruposes it is sufficiently accurate to take

$$\langle s\,|\,\frac{\partial}{\partial y}\,|\,y\rangle = 0.42$$

for all the halogens.

We will calculate δ for Cl_2^-. The internuclear distance R of a free Cl_2^- molecule ion is close to 5.0 a.u.[20] The overlap integrals between two Cl atoms for this separation are[44]

$$S_{\sigma\sigma} = -0.22 \ , \quad S_{\pi\pi} = +0.10$$

and we take

$$S_{\sigma s} \cong -S_{\sigma\sigma} \ ;$$

and therefore

$$\begin{aligned} \mu_u &= (2 + 2S_{\pi\pi})^{-1/2} = 0.67 \ , \\ \beta_u &= (2 + 2S_{\sigma\sigma})^{-1/2} = 0.79 \ , \\ \mu_g &= (2 - 2S_{\pi\pi})^{-1/2} = 0.75 \ , \\ \beta_g &= (2 - 2S_{\sigma\sigma})^{-1/2} = 0.64 \ . \end{aligned} \tag{18}$$

An approximate value $\alpha_u \approx 0.15$ is obtained at the end of Sec. VI from the analysis of the hyperfine components and so, for Cl_2^-, one finds

$$\delta \cong 0.78 \ , \tag{19}$$

which is substantially smaller than the value (16) and shows the importance of including overlap in the calculation.

About 80% in the reduction of the δ value from (16) to (19) comes from the term in (17) involving the gradient integral. This term involves R and α_u, neither of which is as well known as one would like. Jette, Gilbert, and Das[21] have calculated that $R(V_K) > R(\text{free } \mathrm{Cl}_2^-)$ by about 10%. This would reduce the δ value in (19) to about 0.75. However, a comparison of the experimental and calculated hyperfine parameters by the same authors suggests the opposite: $R(V_K) < R(\text{free } \mathrm{Cl}_2^-)$. The accuracy of the value of α_u obtained from the isotropic part of the hyperfine interaction is also doubtful since, among other things, it is not known what the sign and the size of the exchange-polarization contributions are to the isotropic hyperfine interaction. Finally there is very likely an error inherent in the use of the simple LCAO—MO model. Considering everything the error of δ in (19) could be as large as ± 20%.

An experimental δ value can be obtained from the measured g shifts. Because $\lambda_{1u}\lambda'_{1u}\delta \approx 0.6\lambda_{1u}^2$, the following relationship holds between $\Delta g_\parallel \equiv \Delta g_z$ and $\Delta g_\perp = \frac{1}{2}(\Delta g_x + \Delta g_y)$:

$$\Delta g_\perp = 2\delta[-\Delta g_\parallel/(2 - \delta_z)]^{1/2} + 1.6\Delta g_\parallel \ . \tag{20}$$

TABLE VI. Summary of the various energy differences (in eV; see Fig. 1) of the Cl_2^- V_K centers derived from the g shifts and optical-absorption measurements. The values in brackets are the half-widths (in eV) of the optical transitions.

Crystal	$^2\Sigma_u^+ - {^2\Pi_u}$ or $E_{\perp u}$ [a]	Δ_u [a]	$^2\Pi_{u\,3/2} - {^2\Pi_{u\,1/2}}$ or $E_{2u} - E_{1u}$ [a]	$^2\Sigma_u^+ - {^2\Sigma_g^+}$ [b] or E_σ [b]	$\begin{cases} ^2\Sigma_u^+ - {^2\Pi_{g\,3/2}} \\ ^2\Sigma_u^+ - {^2\Pi_{g\,1/2}} \end{cases}$	$^2\Pi_{g\,3/2} - {^2\Pi_{g\,1/2}}$ or $E_{2g} - E_{1g}$	$\lvert\Delta_g\rvert$ [c]
RbCl	2.44	+0.352	0.357	3.40(0.76)	$\cdots$	$\cdots$	$\cdots$
KCl	2.42	+0.119	0.135	3.39(0.81)	$\begin{cases} 1.73^{d} \\ 1.59^{d} \end{cases}$(0.37)	0.14	0.12
NaCl	2.28	−0.344	0.350	3.28(1.12)	$\cdots$	$\cdots$	$\cdots$
LiCl	2.09	−0.580	0.583	3.16(1.47)	$\cdots$	$\cdots$	$\cdots$
Free Cl_2^-	2.91[e]		$\cdots$	3.86[e]	1.87[e]	$\cdots$	

[a] This paper, from the g components.

[b] C. J. Delbecq and P. H. Yuster, results quoted in Ref. 21.

[c] This paper, using (9) with $\lambda'_{1g} = 603\ \text{cm}^{-1} = 0.075$ eV.

[d] From Fig. 5 of Ref. 3.

[e] T. L. Gilbert and A. C. Wahl, Ref. 20.

The accuracy with which δ can be calculated from this relation is almost exclusively dependent upon the accuracy with which $\Delta g_\parallel$ is known. Of the Cl_2^- centers in Table II, the one in KCl has the most accurately determined g_z value. Assuming $\delta_z = 1$, i.e., no appreciable delocalization of the excited $^2\Pi_u$ state, one finds

$$\delta = 0.73 \pm 0.02 . \tag{21}$$

This is reasonably close to the theoretical value given in (19). The δ values for the other chlorides are comparable to this δ value in KCl, but because of the insufficient precision of $\Delta g_\parallel$ in these crystals, not too much weight should be attached to the observed variation of δ.

The situation is different for the Br_2^- centers. The g shifts are more pronounced and $\Delta g_\parallel$ is quite accurately known in this case. Consequently, the observed variation of δ in Table III is distinctly outside experimental error. The average δ value is smaller for Br_2^- than for Cl_2^-. This is reasonable because the Br_2^- internuclear distance R is larger than that of Cl_2^-. Actually, R for Br_2^- is about 10% larger than R of Cl_2^-, and assuming that the overlap integrals for Br_2^- are comparable to those of Cl_2^-, one calculates $\delta = 0.75$ from (17) for Br_2^-. This, as in the case of Cl_2^-, is about 0.05 larger than the experimental value.

One can now determine $E_{\perp u}$, the average energy separation between $^2\Sigma_u^+$ and $^2\Pi_u$. This can be done in two ways: (a) from $\Delta g_\parallel$, or (b) from $\Delta g_\perp$. Explicitly,

$$\lambda_{1u}^2 / E_{\perp u}^2 = -\Delta g_\parallel , \tag{22}$$

$$\frac{\lambda_{1u}}{E_{\perp u}} = \frac{1}{2\delta} \left[\Delta g_\perp - \left(1 + \frac{\mu_u}{\beta_u} \delta \right) \Delta g_\parallel \right] . \tag{23}$$

For the Cl_2^- centers, the $\Delta g_\parallel$ values are presently not accurate enough and $E_{\perp u}$ must be determined from $\Delta g_\perp$ through (23). We have taken the same $\delta = 0.73$ value for the four crystals, and $\lambda_{1u} = 567$ cm^{-1} was determined from (15), (18), and Table V. The resulting $E_{\perp u}$ are given in Table VI. For the Br_2^- centers, $\Delta g_\parallel$ is accurately known, and the $E_{\perp u}$ values in Table VII were derived from (22) using $\lambda_{1u} = 2391$ cm^{-1}. The $E_{\perp u}$ values are believed to be accurate to within ± 5%.

Tables VI and VII also contain the Δ_u and $E_{2u} - E_{1u}$ values. These were obtained as follows. Taking $\delta = \delta_x = \delta_y$ and $\lambda_{1u} = \lambda_{1u,x} = \lambda_{1u,y}$, and ignoring the second-order terms, one derives from (11),

$$g_x - g_y = 2\delta \lambda_{1u} \Delta_u / E_{\perp u}^2 . \tag{24}$$

In other words, the sign and magnitude of the orthorhombic character of the g components depends on the sign and magnitude of the crystalline-field parameters Δ_u. Once Δ_u is known, $E_{2u} - E_{1u}$ is calculated from (8).

Tables VI and VII also include the $^2\Sigma_u^+ - {^2\Sigma_g^+}$ and $^2\Sigma_u^+ - {^2\Pi_g}$ energy differences, obtained from optical-absorption measurements.[2,3,27,45]

For the F_2^- centers, the g_z factors are not accurate enough for even an approximate determination of δ. Taking $R \cong 4$ a.u., we have estimated from (17) that $\delta = 0.77$, and the resulting $E_{\perp u}$ values calculated from (23) are given in Table VIII.

For the I_2^- centers, only g_z and g_y are known, and (because in general $g_y \neq g_x$) this is not sufficient for a determination of δ. However, if one takes $\delta = 0.65$ [estimated with the help of (17), using $R \cong 6$ a.u.] one can calculate $g_\perp$ from $g_\parallel$ [using (20)] and, consequently, g_x can be estimated. These results are included in Tables IV and IX. The $E_{\perp u}$ values of Table IX were calculated from $\Delta g_\parallel$ using $\lambda_{1u} = 4986$ cm^{-1}.

We return to the sign of $g_x - g_y$. For the F_2^- centers (Table I) this quantity is apparently always positive. For the Cl_2^- and Br_2^- V_K centers in the Br_2^--doped alkali chlorides, one observes (Tables II and III) that systematically $g_x - g_y > 0$ in the Rb and K salts, but $g_x - g_y < 0$ in the Na and Li salts. (Our estimates for the I_2^- centers in Table IV sug-

TABLE VII. Same as Table VI, but for the Br_2^- V_K and V_K-type centers.

Crystal	$^2\Sigma_u^+ - {}^2\Pi_u$ or $E_{\perp u}$	Δ_u	$^2\Pi_{u\,3/2} - {}^2\Pi_{u\,1/2}$ or $E_{2u} - E_{1u}$	$^2\Sigma_u^+ - {}^2\Sigma_g^+$ or E_σ	$^2\Sigma_u^+ - {}^2\Pi_{g\,3/2}$ $^2\Sigma_u^+ - {}^2\Pi_{g\,1/2}$	$^2\Pi_{g\,3/2} - {}^2\Pi_{g\,1/2}$ or $E_{2g} - E_{1g}$[a]
RbBr	2.23	+0.196	0.32	•••	•••	•••
KBr	2.19	+0.007	0.25	3.22 (0.73)[b]	1.65 (0.26)[b] ~1.38 (~0.11)[b]	~0.27[b]
NaBr	1.95	−0.425	0.50	3.22 (0.77)[c] 2.58[c,d]	1.58 (0.32)[c] ~1.3 (~0.2)[c]	~0.28[c]
RbCl : Br⁻	2.18	+0.267	0.37	•••	•••	•••
KCl : Br⁻	2.13	+0.060	0.26	•••	•••	•••
NaCl : Br⁻	1.93	−0.358	0.44	•••	•••	•••
LiCl : Br⁻	1.80	−0.572	0.63	•••	•••	•••

[a] The calculated $E_{2g} - E_{1g}$ value from (9) is 0.31 eV − 0.02 eV = 0.29 eV, assuming that Δ_g is small.

[b] From Ref. 3.

[c] C. J. Delbecq and P. H. Yuster (unpublished).

[d] Unidentified absorption.

gest that this behavior is maintained in the iodides.) This change in sign of $g_x - g_y$ is reflected by the change in sign of the crystal field parameter Δ_u in Tables VI, VII, and VIII.

The origin of this sign reversal is not understood, but its existence suggests that a simple crystal field explanation may not be adequate.

The dominant term in the crystal field potential almost certainly derives from the two alkali ions A and B closest to the V_K center, along $y \parallel [1\bar{1}0]$ perpendicular to the molecular axis $z \parallel [110]$ (Fig. 2). For such a situation one expects $g_x - g_y$ to be positive, as the following qualitative argument shows. The electrons in the π_y part of $^2\Pi_g$ have their lobes directed to the positive ions A and B, and have a lower energy than the electrons in π_x whose lobes are oriented along $x \parallel [001]$. Consequently, $E_{1g} \equiv E_x$ is larger than $E_{2g} \equiv E_y$, and since from (11) $\Delta g_x \cong 2\lambda_{1u}/E_y$ and $\Delta g_y \cong 2\lambda_{1u}/E_x$, it follows that $g_x > g_y$. This leaves the data in the Cl and Br salts of Li and Na unexplained.

The next terms in the crystal field potential come from (i) the four halogen ions which are positioned in the plane perpendicular to the V_K-center axis (not shown in Fig. 2), and (ii) the four alkali ions (also not shown in Fig. 2) which are the $\{110\}$ plane containing the V_K-center axis. The four halogen ions, it may be noted, are the ones directly involved in the 60° jump reorientation motion of the V_K center.[10,27] Similar qualitative arguments to the ones given above indicate that the four halogen ions will again give $g_x > g_y$, while the four alkali ions will result in $g_x < g_y$. It would seem then that the sum of these three contributions will give $g_x > g_y$ for the X_2^- centers, while the situation $g_x < g_y$ will not be realized for reasonable distortions of the lattice around the X_2^- molecule ion.

It appears therefore that the sign and magnitude of $g_x - g_y$ could be connected with the degree and nature of the delocalization of the excited $^2\Pi_u$

TABLE VIII. Same as Table VI, but for the I_2^- V_K centers in the alkali iodides.

Crystal	$^2\Sigma_u^+ - {}^2\Pi_u$ or $E_{\perp u}$	Δ_u	$^2\Pi_{u\,3/2} - {}^2\Pi_{u\,1/2}$ or $E_{2u} - E_{1u}$	$^2\Sigma_u^+ - {}^2\Sigma_g^+$ or E_σ	$^2\Sigma_u^+ - {}^2\Pi_{g\,3/2}$ $^2\Sigma_u^+ - {}^2\Pi_{g\,1/2}$	$^2\Pi_{g\,3/2} - {}^2\Pi_{g\,1/2}$ or $E_{2g} - E_{1g}$
RbI[a]	2.12	(+0.20)[b]	0.56	3.06 (0.50) 2.21[d] (0.33)	1.56 (0.22) ~1.11	0.45[c]
KI[e]	2.03	(+0.03)[b]	0.53	3.10 (0.55) 2.12[d] (0.36)	1.55 (0.19) 1.08	0.47[c]
NaI[a]	1.68	(−0.10)[b]	0.53	2.87 (0.90) 2.03[d] (0.47)	1.41 •••	•••

[a] The optical data for RbI and NaI are from Ref. 26.

[b] Assuming that our estimate of g_x in Table IV is correct.

[c] The calculated $E_{2g} - E_{1g}$ value from (9) is 0.66 − 0.16 eV = 0.54 eV assuming that Δ_g is small.

[d] Unidentified absorption.

[e] Optical data for KI from Ref. 3.

TABLE IX. Same as Table VI but for the F_2^- V_K center in the alkali fluorides.

Crystal	$^2\Sigma_u^+ - {^2\Pi_u}$ or E_{1u}	Δ_u	$^2\Sigma_u^+ - {^2\Sigma_g^+}$ or E_σ	$^2\Sigma_u^+ - {^2\Pi_g}$ or E_{1g}
KF	2.55	~ +0.2	···	···
NaF	2.41	~ +0.1	3.38 (0.66)	···
LiF	2.38	~ +0.1	3.48 (1.20)	1.65
Free F_2^- [a]	3.70		4.74	2.23

[a] T. L. Gilbert and A. C. Wahl, Ref. 20.

states. One expects delocalization effects to be more prominent in crystals with (a) a small lattice parameter and (b) the larger and therefore more polarizable halogen ions. Inspection of Tables II–IV shows indeed that $g_x < g_y$ in the Cl, Br, and I salts of Li and Na. In Sec. VII where the V_{KA}, V_{KAA}, and V_F centers are discussed, we will briefly return to the sign of $g_x - g_y$.

Finally, a word should be said about the transitions labeled "unidentified" in Tables VII and VIII. Such a transition was first observed at 2.12 eV in KI by Delbecq, Hayes, and Yuster,[3] and was later also observed in NaI, RbI,[27] and NaBr. It was suggested that this absorption might be caused by a $^2\Sigma_u^+ \rightarrow {^2\Pi_u}$ transition made allowed because of odd lattice modes. Our determination of the $^2\Sigma_u^+ - {^2\Pi_u}$ energy differences from the g shifts shows that there is reasonable agreement with the unidentified absorption bands in the case of RbI and KI. There is a discrepancy the case of NaI (1.68 vs 2.03 eV) and it is very distinct in NaBr (1.95 vs 2.58 eV). These discrepancies do not support the proposed $^2\Sigma_u^+ \rightarrow {^2\Pi_u}$ assignment of the transition. We are at this point more inclined to believe that the approximate agreement in KI and RbI is accidental, and that another explanation for the observed transition may have to be considered.

VI. HYPERFINE COMPONENTS

The Hamiltonian describing the hyperfine interaction of the n valence electrons with the nucleus of an atom k is[46]

$$\mathcal{H}_{\mathrm{HF},k}^{\mathrm{atom}} = \sum_{i=1}^{n} g_0 \mu_B \frac{\mu_{N,k}}{I_k} \left[\langle r_i^{-3} \rangle_s \left(3 \frac{(\vec{\mathrm{r}}_{i,k} \cdot \vec{\mathrm{I}}_k)(\vec{\mathrm{r}}_{i,k} \cdot \vec{\mathrm{s}}_i)}{r_i^2} - \vec{\mathrm{s}}_i \cdot \vec{\mathrm{I}}_k \right) + \langle r_i^{-3} \rangle_c \, \vec{\mathrm{s}}_i \cdot \vec{\mathrm{I}}_k + \langle r_i^{-3} \rangle_l \, \vec{\mathrm{l}}_{i,k} \cdot \vec{\mathrm{I}}_k \right], \quad (25)$$

in which $g_0 = 2.0023$ is the free-electron g factor, μ_B the Bohr magneton, $\mu_{N,k}$ and I_k the nuclear moment and nuclear spin of the nucleus, and $\vec{\mathrm{r}}_{i,k}$ and $\vec{\mathrm{l}}_{i,k}$ the position vector and orbital angular moment of electron i with respect to the nucleus. The summation is over all the equivalent valence electrons.

The first two terms in (25) describe the dipole-dipole interaction between the magnetic moments of the electrons and nucleus. The third term is the isotropic Fermi-contact term and the last term represents the interaction between the orbital moment of the electrons and the nucleus.

Form (25) allows one to calculate the atomic hf effects using simple determinantal wave functions constructed from restricted Hartree–Fock one-electron functions. The many-electron effects (core polarization and configuration interaction) and the relativistic effects are absorbed in the $\langle r^{-3} \rangle_s$, $\langle r^{-3} \rangle_l$, and $\langle r^{-3} \rangle_c$ parameters.

For the description of the hyperfine effects of the X_2^- molecule ions, the following effective oper-

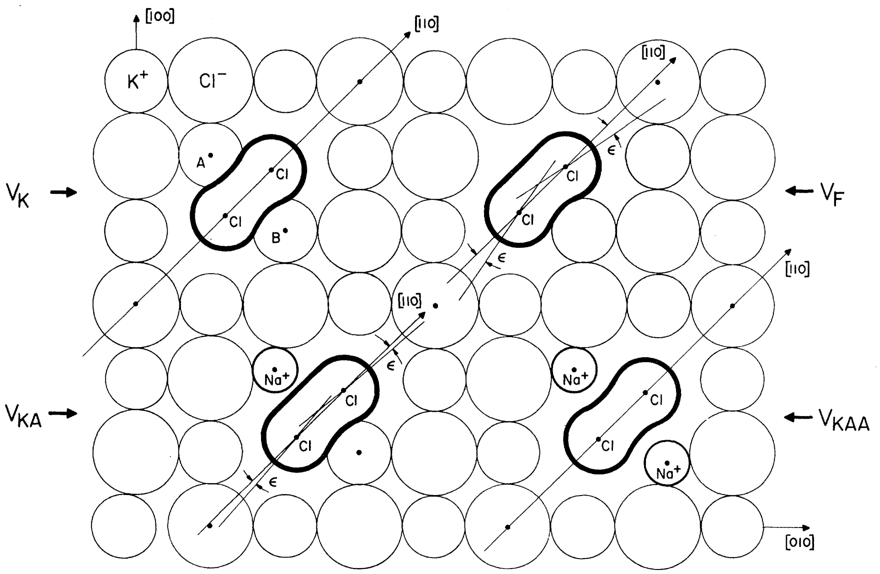

FIG. 2. Schematic models of the V_K, $V_{KA}(\mathrm{Na}^+)$, $V_{KAA}(\mathrm{Na}^+)$, and V_F centers in KCl.

ator will be used[47]:

$$\mathcal{H}^{\text{mol}}_{\text{HF}} = \sum_{k=1}^{2} \mathcal{H}^{\text{atom}}_{\text{HF},k} \; . \tag{26}$$

The summation is over the two nuclei, and $\mathcal{H}^{\text{atom}}_{\text{HF},k}$ is given by (25). In doing so one makes a number of approximations. What is defined as the valence configuration of X_2^-, namely, (2), is not made up of equivalent electrons. Calculation of the hf components including higher-order hf effects involves matrix elements of a molecular hf operator within σ_u, between σ_u and π_u and within π_u. In principle, each of these matrix elements should be characterized by a different set of $\langle r^{-3}\rangle_s$, $\langle r^{-3}\rangle_l$, and $\langle r^{-3}\rangle_c$ parameters. The resulting expressions for the hf components would contain too many parameters and would not be useful. The approximation implicit in (26) consists in equating all the different $\langle r^{-3}\rangle_s$ parameters with each other, with a similar implication for $\langle r^{-3}\rangle_l$ and $\langle r^{-3}\rangle_c$. Such an approximation seems reasonable for the $\langle r^{-3}\rangle_s$ and $\langle r^{-3}\rangle_l$ parameters, because the X_2^- valence configuration (2) is built up from the equivalent p electrons of X^- and X^0. It is probably not reasonable to equate all the $\langle r^{-3}\rangle_c$ parameters. However, if one carries the calculation through using different $\langle r^{-3}\rangle_c$ parameters, one finds that, except for the $\langle r^{-3}\rangle_c$ parameter in the ground state σ_u, these parameters are of little quantitative consequence because they occur in very small higher-order correction terms. Therefore only the $\langle r^{-3}\rangle_c$ parameter within σ_u will be retained. In spite of these approximations one hopes the use of (26) introduces a genuine improvement in the accuracy of the expressions for the hyperfine components which are derived from it. The actual calculation of these components is somewhat tedious but straightforward. One calculates the combined effect of the spin-orbit interaction and the hf operator to second order, and the hf components are then given by the coefficients of the terms linear in the product of the components of $\vec{S}$ and $\vec{I}$. One finds in an axial approximation $(\lambda_{1u} > 0)$:

$$\begin{aligned} A_{\parallel} &= A_\sigma + 2\rho_s - 3\,\frac{\lambda_{1u}}{E_{\perp u}}\,\frac{\mu_u}{\beta_u}\,\rho_s - \frac{1}{2}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,A_\sigma + \frac{5}{2}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\frac{\mu_u^2}{\beta_u^2}\,\rho_l + 2\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\frac{\mu_u^2}{\beta_u^2}\,\rho_s - \frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\rho_s \; , \\ A_{\perp} &= A_\sigma - \rho_s + 5\,\frac{\lambda_{1u}}{E_{\perp u}}\,\frac{\mu_u}{\beta_u}\,\rho_s + \frac{3}{2}\,\frac{\lambda_{1u}}{E_{\perp u}}\,\frac{\mu_u}{\beta_u}\,\rho_s - \frac{1}{2}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,A_\sigma - \frac{5}{2}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\frac{\mu_u^2}{\beta_u^2}\,\rho_l - \frac{3}{4}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\frac{\mu_u^2}{\beta_u^2}\left(\frac{\mu_u}{\beta_n} + 2\right)\rho_s + \frac{1}{2}\,\frac{\lambda_{1u}^2}{E_{\perp u}^2}\,\rho_s \; , \end{aligned} \tag{27}$$

in which

$$\begin{aligned} A_\sigma &= \tfrac{8}{3}\pi(\mu_N/I)\alpha_u^2\langle r^{-3}\rangle_c \; , \\ \rho_s &= \tfrac{2}{5}\,(\mu_N/I)\beta_u^2\langle r^{-3}\rangle_s \; , \\ \rho_l &= \tfrac{2}{5}\,(\mu_N/I)\beta_u^2\langle r^{-3}\rangle_l \; . \end{aligned} \tag{28}$$

Expressions (27) can be rewritten as a function of the experimental g shifts, using (22) and (23). The recognition that a term is a first-order or a second-order correction term can be maintained, by expressing $\lambda_{1u}/E_{\perp u}$ as a function of primarily $\Delta g_\perp$, and $\lambda_{1u}^2/E_{\perp u}^2$ as a function of $\Delta g_\parallel$. If one substitutes (22) and (23) into (27) and furthermore takes $\mu_u/\beta_u = 1$ and $\delta = 1$, one finds the expressions derived by Jette.[21,48] The relationship between Jette's notation and ours is $a_F = A_\sigma$ and $b = 3\rho_s \equiv 3\rho_l$.

$\Delta g_\perp$ and $\Delta g_\parallel$ are known experimentally and if we assume that we know μ_u and β_u [see (18)], then $A_\parallel$ and $A_\perp$ are still functions of three unknown parameters. It is our aim to determine ρ_s and A_σ, and therefore we will make an assumption about ρ_l since it enters in the higher-order correction terms.

The experimental and theoretical results obtained so far[49] suggest the following rule:

$$\langle r^{-3}\rangle_l < \langle r^{-3}\rangle_{\text{HF}} < \langle r^{-3}\rangle_s \; ,$$

with

$$\langle r^{-3}\rangle_{\text{HF}} \approx \tfrac{1}{2}\left[\langle r^{-3}\rangle_l + \langle r^{-3}\rangle_s\right] \; , \tag{29}$$

in which $\langle r^{-3}\rangle_{\text{HF}}$ is the value calculated using the restricted Hartree–Fock one-electron function. Quantitatively, for many of the atomic[50,51] and molecular[52] systems it has been found that

$$\langle r^{-3}\rangle_s / \langle r^{-3}\rangle_l = 1.13 \pm 0.05 \; . \tag{30}$$

This is so for the F atom,[50] and we will assume in this paper that the same ratio holds approximately for Cl, Br, and I. We will furthermore accept that $\delta = 0.70$ and $\mu_u/\beta_u = 0.85$ for all X_2^- molecule ions. With these assumptions, expressions for $A_\parallel$ and the $A_\perp$ applicable to all X_2^- can be written

$$\begin{aligned} A_\parallel &= A_\sigma + 2\rho_s + (-1.81\Delta g_\perp + 0.86\Delta g_\parallel)\rho_s + \tfrac{1}{2}\Delta g_\parallel A_\sigma \; , \\ A_\perp &= A_\sigma - \rho_s + (3.58\Delta g_\perp - 2.14\Delta g_\parallel)\rho_s + \tfrac{1}{2}\Delta g_\parallel A_\sigma \; . \end{aligned} \tag{31}$$

Clearly, the numerical coefficients will vary somewhat, not only for the same X_2^- throughout a series of AX crystals, but also for the different X_2^- molecule ions. However, calculation or estimation of these variations is rather involved and falls outside the scope of this paper.

In order to analyze the hf components of Tables II–IV with formulas (31), one needs to know the

TABLE X. Isotropic part A_σ and the anisotropic part ρ_s (both in G) of the hyperfine interaction of the various X_2^- V_K centers.

Crystal	$X_2^- \equiv F_2^-$ ρ_s	A_σ	$X_2^- \equiv Cl_2^-$ ρ_s	A_σ	$X_2^- \equiv Br_2^-$ ρ_s	A_σ	$X_2^- \equiv I_2^-$ ρ_s	A_σ
RbX	···	···	32.4	39.6	178.0	151.3	204	109
KX	312	284	32.3	39.1	179.8	144.5	207	99
NaX	315	268	32.6	36.0	182.3	126.6	216	61
LiX	315	257	32.3	33.6	···	···	···	···
RbCl : Br^-					177.8	152.3		
KCl : Br^-					179.5	146.4		
NaCl : Br^-					183.6	128.2		
LiCl : Br^-					185.3	114.6		
Free X_2^{-}[a]	314[b]	226.3	30.2[b]	27.1	···	···	···	···

[a] From Ref. 21. For F_2^-: $R=3.6$ a.u. and for Cl_2^-: $R=5.0$ a.u.

[b] Assuming $\langle r^{-3}\rangle_{HF} \cong \frac{1}{2}[\langle r^{-3}\rangle_s + \langle r^{-3}\rangle_l]$.

signs of $A_\parallel$ and $A_\perp = \frac{1}{2}(A_x + A_y)$. The nuclear moments of all the halogen nuclei are positive, and it follows from (27) and (28) that $A_\parallel$ has a positive sign. The sign of $A_\perp$ presents a problem, however. It was proposed earlier by the author[53] that $A_\perp > 0$ for Cl_2^-, Br_2^-, and I_2^- and $A_\perp < 0$ for F_2^-. The determination in this paper of the orthorhombic character of the g and hf tensors allows us to present more direct evidence that indeed $A_\parallel > 0$, $A_\perp > 0$ for Cl_2^- and Br_2^-, and by inference substantiate the choice made for I_2^- and F_2^- in Tables I and IV.

Expressions (27) were derived in an axial approximation but if this restriction is dropped, it is easy to show that, to first order,

$$A_x = A_\sigma - \rho_s + \tfrac{5}{2}\,\Delta g_x \,\frac{\mu_u}{\beta_u}\,\frac{1}{\delta}\,\rho_l + \tfrac{3}{4}\,\Delta g_y\,\frac{\mu_u}{\beta_u}\,\frac{1}{\delta}\,\rho_s\ ,$$

with a similar expression for A_y, obtained by exchanging Δg_x and Δg_y. Consequently,

$$\Delta A_\perp = \tfrac{1}{2}(A_x - A_y) = (g_x - g_y)\tfrac{7}{8}\rho_s\,\frac{\mu_u}{\beta_u}\,\frac{1}{\delta}\ , \qquad (32)$$

if we put $\rho_l = \rho_s$. Therefore, if this mechanism is the only, or dominant, source of the orthorhombic character of the $\vec{A}$ tensor, then $\Delta A_\perp$ must possess the same sign as $g_x - g_y$. Inspection of the Cl_2^- and Br_2^- data in Tables II and III shows that (32) is fulfilled in all cases, if indeed $A_\perp = \frac{1}{2}(A_x + A_y)$ is positive for these molecule ions. Quantitatively, however, the experimental $\Delta A_\perp$ values in Tables II and III are consistently smaller than the ones calculated from (32). This may indicate that there is another mechanism contributing to the orthorhombic character (e.g., a distortion of the orbitals by the crystal field). It is also possible that there is a systematic error in the experimental determination of $\Delta A_\perp$, which is a subtle and small quantity.

Table X contains results of the hf analysis. One observes that for both Cl_2^- and Br_2^-, ρ_s remains approximately constant while A_σ increases by as much as 20% in going from the Li to the Rb salt. Such a behavior was considered to be the most reasonable one on empirical grounds in Ref. 53. Furthermore, Jette, Gilbert, and Das[21] have calculated that a change of the internuclear X_2^- distance affects A_σ much more strongly than ρ_s.

Actually, ρ_s for Br_2^- shows some change. However, considering all the approximations leading to (31) we are hesitant to state whether or not the sense and the magnitude of this change in ρ_s is at all meaningful. We are more inclined to believe that the spread in ρ_s values in Table X should be looked upon as a measure of the accuracy of the present analysis. Assuming that A_σ and ρ_s of F_2^- and I_2^- should behave in the same way as in the case of Cl_2^- and Br_2^-, one can establish the sign of $A_\perp$ for F_2^- and I_2^-. Doing the analysis for both signs of $A_\perp$ establishes convincingly that $A_\perp < 0$ for F_2^- and $A_\perp > 0$ for I_2^-. Table X includes the results of this hf analysis.

The results of Table X can be used to calculate the amount of s character, α_u^2, and the amount of p character, β_u^2, of the ${}^2\Sigma_u^+$ ground state. From (28), (29), and Table V, one calculates that the $\rho_s = 32.4$ G value of Cl_2^- corresponds to $\beta_u = 0.81$, which is in good agreement with (18). The $A_\sigma = 39.1$-G value for Cl_2^- in KCl corresponds to [assuming $\langle r^{-3}\rangle_c \equiv |\psi_{3s}(0)|^2$] $\alpha_u \cong 0.15$ and this value was used in the calculation of δ from (17).

VII. SELECTED RESULTS FOR V_{KA}, V_{KAA}, AND V_F CENTERS

In Secs. I–VI we have dealt with the variation of the EPR and optical-absorption parameters of the V_K and V_K-type X_2^- centers throughout the otherwise unperturbed alkali-halide lattices. It seems appropriate in this context to present some experimental results on V_{KA}, V_{KAA}, and V_F centers in KCl and NaCl.[7] The schematic models of these centers in KCl are presented in Fig. 2. These models are believed to be correct and no attempt will be made to justify them here. The V_{KA}, V_{KAA}, and V_F centers may be considered as V_K centers for which the surrounding lattice has been changed in a distinct and well-defined way. A V_F center is a V_K center for which one of the two closest K^+ ions has been taken away. In the V_{KA} centers the same K^+ ion has been replaced by a smaller Na^+ or Li^+ ion, and in $V_{KAA}(Na^+)$ the two closest K^+ ions are replaced by Na^+ ions.

A V_K-center theory which is flexible enough should be able to describe the changes in the EPR and optical-absorption results brought about by these distinct changes in the V_K-center environment. Conversely, the availability of systematic experimental data for the V_{KA}, V_{KAA}, and V_F centers may contain clues as to which aspects of the environment are dominant in influencing the V_K-

TABLE XI. Spin-Hamiltonian parameters at 77 K and some thermal data of the V_F-, V_{KA}-, and V_{KAA}-type $^{35}Cl_2^-$ centers (see Fig. 2) in KCl and NaCl.

Crystal	Center	g_z [110]	g_x [001]	g_y [$1\bar{1}0$]	A_z [110]	$A_\perp = \frac{1}{2}(A_x+A_y)$	$\Delta A_\perp = \frac{1}{2}(A_x-A_y)$	Bending angle ϵ	ΔH	T_{decay} T_{dis}
KCl : Pb^{++}	V_F[a]	2.0015 ± 0.0002	2.0439 ± 0.0003	2.0414 ± 0.0003	+103.8 ± 0.1	+14.9	⋯	1.5°	2.0 ± 0.3	240[b] 112[b]
NaCl : Pb^{++}	V_F[a]	2.0015 ± 0.0002	2.0428 ± 0.0004	2.0483 ± 0.0004	+104.0 ± 0.2	+15.0	⋯	3.2°	6.0 ± 0.5	~ 230[c] ⋯
KCl : Na$^+$	$V_{KA}(Na^+)$[d]	2.0015 ± 0.0002	2.0394 ± 0.0002	2.0426 ± 0.0002	+102.59 ± 0.05	+12.65	−0.37	$\lesssim$ 0.2°	3.5 ± 0.5	265[c] 165[c]
KCl : Na$^+$	$V_{KAA}(Na^+)$[d]	2.0015 ± 0.0002	2.0364 ± 0.0002	2.0409 ± 0.0002	+103.29 ± 0.10	+15.75	−1.27	0°	6.0 ± 0.5	280[c]
KCl : Li$^+$	$V_{KA}(Li^+)$[d]	2.0015 ± 0.0002	2.0367 ± 0.0002	2.0399 ± 0.0002	+102.95 ± 0.05	+15.76	−0.78	< 0.2°	3.1 ± 0.5	310[c] 133[c]
NaCl : Li$^+$	$V_{KA}(Li^+)$[a]	2.0015 ± 0.0002	2.0395 ± 0.0004	2.0462 ± 0.0004	+100.6 ± 0.1	+12.2	⋯	< 0.2°	5.6 ± 0.5	235[c] < 65[c]

[a] Results obtained by a perturbation solution (Ref. 9) of spin Hamiltonian (1).

[b] C. J. Delbecq, D. Schoemaker, and P. H. Yuster (unpublished).

[c] D. Schoemaker (unpublished).

[d] These EPR parameters were obtained by a computer analysis of spin Hamiltonian (1). It was assumed that $P = -4.87$ G in all cases.

center properties, both electronic and motional.

The EPR data of the V_F, V_{KA}, and V_{KAA} centers in KCl and NaCl are given in Table XI. The V_{KA} centers, and especially the V_F centers, exhibit a small bending of the molecular bond. In principle this will result in a first-order contribution to Δg_z. However, the bending is so small that this first-order contribution can be entirely neglected for our purposes. The g-factor formula (23) and the hyperfine formulas (31) are then immediately applicable to these centers. The first three rows in Table XII contain results derived from the perpendicular g components g_x and g_y. For this analysis the assumption was made that $\delta = 0.73$; this was the value used for the Cl_2^- V_K centers. The last row gives the energies of the $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transitions as far as they are known. No experimental results exist as yet for the $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transitions of these centers. Finally, Table XIII gives the results of the analysis of the hf components. Comparison of Tables XI–XIII with corresponding Tables II, VI, and X shows that (i) the hf interaction is increased and (ii) the perpendicular g shift $\Delta g_\perp = g_\perp - g_0$ is reduced for the V_F, V_{KA}, and V_{KAA} centers compared to the corresponding V_K centers. From Table XIII it is seen that the change in hf interaction is almost exclusively caused by a change in the isotropic part A_σ of the hf tensor.

If one plots $\Delta g_\perp$ vs A_σ (Fig. 3) for all the Cl_2^- centers, one observes that the points corresponding to the V_K, V_{KA}, and V_{KAA} centers are scattered very closely along a straight line described

TABLE XII. Summary of the various energy differences in eV (see Fig. 1) of the V_{KA}, V_{KAA}, and V_F centers in KCl and NaCl, derived from the g shifts and the optical-absorption measurements. The half-width (in eV) is given between brackets.

Crystal	Center	$^2\Sigma_u^+ - {}^2\Pi_u$ or $E_{\perp u}$[a]	Δ_u	$^2\Pi_{u3/2} - {}^2\Pi_{u1/2}$ or $E_{2u} - E_{1u}$	$^2\Sigma_u^+ - {}^2\Sigma_g^+$ or E_σ
KCl:Pb^{++}	V_F	2.46	+0.09	0.11	3.44 [0.74][b]
KCl:Na$^+$	$V_{KA}(Na^+)$	2.57	−0.21	0.22	3.49 [0.85][c]
KCl:Na$^+$	$V_{KAA}(Na^+)$	2.67	−0.31	0.32	...
KCl:Li$^+$	$V_{KA}(Li^+)$	2.75	−0.24	0.25	3.52 [0.79][c]
NaCl:Pb^{++}	V_F	2.30	−0.28	0.29	3.32[c]
NaCl:Li$^+$	$V_{KA}(Li^+)$	2.45	−0.39	0.40	3.40[c]

[a] From (23) assuming that $\delta = 0.73$ in all cases.

[b] C. J. Delbecq, D. Schoemaker, and P. H. Yuster (unpublished)

[c] D. Schoemaker (unpublished).

TABLE XIII. The isotropic part A_σ and the anisotropic part ρ_s or the hyperfine interaction of the V_F, V_{KA}, and V_{KAA} Cl_2^- centers in KCl and NaCl.

Crystal	Center	ρ_s	A_σ
$KCl:Pb^{++}$	V_F	31.9	42.3
$KCl:Na^+$	$V_{KA}(Na^+)$	32.2	40.4
$KCl:Na^+$	$V_{KAA}(Na^+)$	31.2	42.9
$KCl:Li^+$	$V_{KA}(Li^+)$	31.0	42.9
$NaCl:Pb^{++}$	V_F	32.1	42.3
$NaCl:Li^+$	$V_{KA}(Li^+)$	31.8	39.3

by

$$\Delta g_\perp = -0.00115 A_\sigma + 0.0855 \qquad (33)$$

However, the V_F-center points deviate very strongly from this line. The absence of, e.g., a K^+ ion (i.e., the presence of a positive-ion vacancy) in the case of the V_F center in KCl, appears to be a much larger perturbation on the Cl_2^- molecule ion than replacing K^+ by Na^+ or Li^+ as in the case of $V_{KA}(Na^+)$ and $V_{KA}(Li^+)$. The large deviation of the V_F-center points from (33) is therefore, in some intuitive way, not surprising.

However, one may ask whether a relation such as (33) has a physical basis. It has if one can assume that the primary effect of the lattice on the Cl_2^- molecule ion is to change the Cl_2^- internuclear distance. Both A_σ and $\Delta g_\perp$ (the latter through $E_{\perp u}$) are dependent on R in the free Cl_2^- molecule ion,[20,21] and consequently, to a first approximation, a linear relation such as (33) appears to be quite reasonable. Since both A_σ and $E_{\perp u}$ decrease with increasing R,[21] one would have to conclude that the Cl_2^- internuclear distance of $V_{KA}(Li^+)$ in KCl is the smallest, and that of the V_K center in LiCl the largest. More specifically still, $R(V_K;\ \text{LiCl}) > R(V_K;\ \text{RbCl})$ which, if true, would be in contradiction to the calculations of Jette, Gilbert, and Das.[21]

The fact that the V_F-center points are not approximated by (33) suggests that the description of the change of the EPR parameters solely in terms of a varying interncuelar distance is very likely a too simple one. Still, it is possible that the description could have a qualitative validity for certain sets of not too different centers such as the V_K, V_{KA}, and V_{KAA} centers. It has also been used routinely in discussing the H and H-type center parameters.[11,15,16]

Comparison of Tables XI and II yields another interesting observation. The V_F-center g components show only a small reduction in the value of $\Delta g_\perp = \frac{1}{2}(\Delta g_x + \Delta g_y)$, and, more importantly, the sign and magnitude of $g_x - g_y$ are maintained compared with the V_K center. For the supposedly less-strongly-perturbed $V_{KA}(Na^+)$ and $V_{KA}(Li^+)$ centers in KCl one observes, apart from a more pronounced reduction of $\Delta g_\perp$, a complete reversal of the sign of $g_x - g_y$. This sign reversal is illustrated by the change in sign of the crystal field parameters Δ_u in Tables XII and VI. It is not immediately obvious why, on the one hand, a vacancy has such a modest and, on the other hand, the Na^+ or Li^+ ions (in KCl) have such a drastic influence on the sign and magnitude of $g_x - g_y$. In this connection, and also in connection with the discussion based on Fig. 3, it could be of interest to study systematically the V_F, V_{KA}, and V_{KAA} centers in a large number of appropriately doped alkali halides. Many of these centers have already been observed and analyzed in a number of alkali bromides,[7] but the EPR parameters (especially the perpendicular parameters A_x, A_y, g_x, and g_y), have not been determined with sufficient precision to warrant their inclusion here.

Finally, in contrast to the V_K center, the reorientation and decay mechanisms are distinct from one another in the case of the V_F and V_{KA} centers. Table XI includes the disorientation temperatures and the decay temperatures. The structure of $V_{KAA}(Na^+)$ does not permit any reorientation. It shares this property with the H_{AA} center.[17]

VIII. CONCLUSION

A careful analysis of the EPR parameters combined with optical-absorption and thermal data has yielded a large amount of detailed quantitative information on the ground and excited states of the V_K centers and related centers. Many trends and regularities in the parameters are observed. However, the understanding and quantitative description of the behavior of many of the V_K-center parameters is still incomplete and tentative. It is clear that much more experimental and theoretical work will be needed before one reaches an understanding of the V_K-center electronic structure which is comparable to that other well-known center in the alkali halides, the F center.

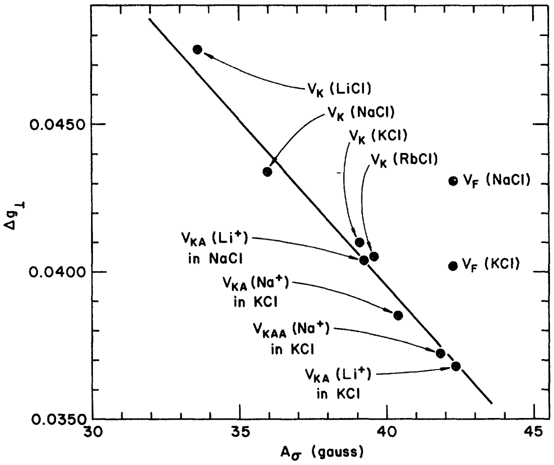

FIG. 3. Plot of $\Delta g_\perp$ vs A_σ for various Cl_2^- centers in the alkali chlorides.

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