Interstitial and di-interstitial $BrCl_2{}^{2-}$ in KCl[†]

Dirk Schoemaker and Ad Lagendijk
*Physics Department, University of Antwerp (UIA), 2610-Wilrijk, Belgium**
and Argonne National Laboratory, Argonne, Illinois 60439

(Received 21 January 1977)

In KCl crystals containing both Na^+ and Br^- ions as impurities, three types of $(ClBrCl)^{2-}$ centers are identified by ESR after x irradiation at 77 K followed by a suitable thermal treatment. The first $BrCl_2{}^{2-}$ is [110] oriented and possesses C_{2v} symmetry. It is an $H_A(Na^+)$-type center: the Br occupies the interstitial position between two substitutional Cl along [110] and next to the Br is a substitutional Na^+ impurity along $[1\bar{1}0]$ which induces a bending of the molecule of about 14°. The second $BrCl_2{}^{2-}$ is also oriented along [110] but possesses D_{2h} symmetry. It is an $H_{AA}(Na^+)$-type center: the interstitial Br is now flanked by two Na^+ impurities along $[1\bar{1}0]$. These two centers, which may be considered as impurity stabilized interstitial bromine atoms Br_i^0, are thought to be formed by the trapping of a mobile Cl_i^0 by a pair of substitutional Br^- and Na^+ ions, or by a complex of two Na^+ ions adjoining a Br^-, respectively. The third $BrCl_2{}^{2-}$ has C_{1h} symmetry. It is a di-interstitial center: the $BrCl_2{}^{2-}$ occupies a single negative-ion site next to a substitutional Na^+ impurity and the molecular axis makes a 22° angle with $\langle 100\rangle$ in a $\{110\}$ plane. The latter center is thought to be formed by the trapping of both a Cl_i^0 and a Cl_i^- by a pair of adjoining substitutional Br^- and Na^+ ions. A short discussion of the $BrCl_2{}^{2-}$ electronic structure is given.

I. INTRODUCTION

The fundamental paramagnetic interstitial center in the alkali halides is the *H* center. It consists of a diatomic halogen molecule ion X_2^- occupying a single negative ion site. It is $\langle 110\rangle$ oriented in KCl and KBr,[1,2] and $\langle 111\rangle$ oriented in LiF.[3] From a chemical point of view the *H* center is an interstitial halogen atom X_i^0 which has formed a molecular bond with a substitutional halogen ion X_s^-.[4,5]

In KCl the *H* center starts to diffuse (and decay) above 40 K. This motion of the *H* center has two components. First, there is the motion in which the interstitial Cl_i^0 jumps to a neighboring site along $\langle 110\rangle$ reforming a Cl_2^- on the new site. The second motion, which starts already at 11 K,[2,6] is a reorientation motion of the Cl_2^- on its site among the six possible $\langle 110\rangle$ directions. Both motions occur above 40 K and assure a random diffusion of the interstitial, i.e., the *H* center.

If the alkali halide contains a small amount of impurity ions it is observed that many of them can stabilize the diffusing interstitial to higher temperatures. Two classes of impurities have been studied in particular, namely, foreign halogen ions and foreign alkali ions. When mobile *H* centers are trapped in the immediate vicinity of the latter, H_A,[7-9] H_{AA}, and $H_{A'A}$,[10] centers are formed.

Trapping by foreign halogen ions has been studied in the case of KCl and KBr containing the small F^- ion as a substitutional impurity.[11-13] Trapping of the *H* center by these results in the formation of $\langle 111\rangle$ oriented FCl^- and FBr^- molecule ions occupying a single negative-ion site. One may consider these centers as representing the interstitial fluorine atom F_i^0 center, although it should be emphasized immediately that this and similar descriptions later on are little more than a schematic way of talking about interstitial halogen molecule-ion centers.

Trapping of a mobile Cl_i^0 by the small F_s^- ion appeals to the intuition because in forming FCl^- the strain energy associated with the interstitial is lowered. However, stabilization of a Cl_i^0 in KCl by a larger substitutional halogen ion such as Br^- or I^- should not be excluded *a priori*, because stabilization of an interstitial involves a subtle interplay between ionic and electronic effects. Such Br^- or I^- stabilized Cl_i^0 centers, whatever the actual size and shape of the resulting halogen molecule ion, may be considered to represent the Br_i^0 or I_i^0 centers in KCl.

The present paper discusses Br_i^0 and I_i^0 centers. To be sure, we have not detected the pure Br_i^0 or I_i^0 centers, but we have found impurity trapped Br_i^0 and I_i^0 in KCl. It may be that failure to observe the pure Br_i^0 center so far may be due to an experimental limitation, namely, that the crystals could not be x or γ irradiated below 77 K with our experimental setup.

It will be shown (Secs. II–V) that at 77 K, Br_i^0 can be stabilized either next to a single substitutional Na^+, or between pairs of substitutional Na^+, and that in both cases the Br_i^0 manifests itself as $\langle 110\rangle$ oriented $BrCl_2{}^{2-}$ molecule ions in a $(ClBrCl)^{2-}$ configuration. In the course of these studies a third $BrCl_2{}^{2-}$ was observed which is ascribed to a di-interstitial-type center (Sec. VI). In Sec. VII a short discussion of the electronic structure of

$BrCl_2^{2-}$ is presented. Li^+-stabilized Br_i^0 and I_i^0 centers in KCl have been described before.[14]

II. EXPERIMENTAL

The KCl crystals were grown in air by the Kyropoulos method. They were doped either with Br^- (or I^-) alone, or with Br^- (or I^-) and Na^+ together. The doping concentrations of each impurity could be "high" or "low" corresponding to doping concentrations in the melt of 1 or 0.1 mol%, respectively. The four possible combinations of "high" and "low" were grown and studied. The ESR spectra were taken with Varian spectrometers (V-4500 and E-12). All x irradiations were performed at 77 K using a tungsten tube operating at 50 kV and 50 mA. The irradiation times were usually several hours. Optical excitations were performed using a 250-W high-pressure mercury lamp with appropriate cutoff and interference filters.

III. PRODUCTION OF THE $BrCl_2^{2-}$ CENTERS

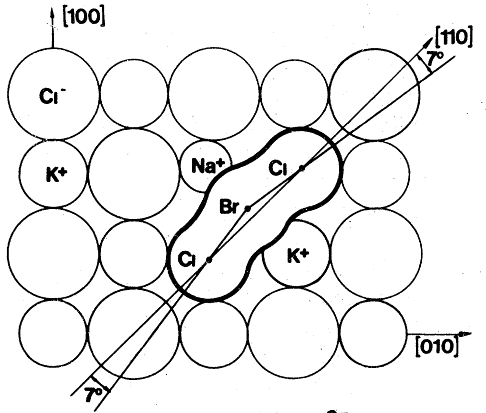
Because the original aim was to produce the pure Br_i^0 center, KCl crystals with various Br^- concentrations were x irradiated and studied with ESR at 77 K. The expectation was that the mobile Cl_i^0 centers (H centers) created by the irradiation would be trapped by the substitutional Br^- impurity forming an H-type Br_i^0 center. By analogy with the H center itself one might expect that such a center would manifest itself as a $BrCl^-$ molecule ion which might be either ⟨110⟩ or ⟨111⟩ oriented.

Other than the ESR signals of the F center and the V_K-type Cl_2^-,[15,16] $BrCl^-$,[17] and $^{16}Br_2^-$ (the latter with very low concentration) centers, no other ESR signals were observed at 77 K in these KCl:Br^- crystals even after many hours of x irradiation. However, in certain of the heavily Br^--doped KCl samples, and after very long irradiation times, sometimes a very weak ESR signal was observed originating from a $BrCl_2^{2-}$ molecule in the symmetric $(ClBrCl)^{2-}$ configuration. That this was very likely an interstitial halogen-atom–type center and not a trapped hole-type center, was supported by the observation that optical excitation of F and F' centers, a process which produces mobile electrons in the lattice, did not result in a noticeable decrease of the intensity of this $BrCl_2^{2-}$, while the positively charged V_K-type centers were wiped out very quickly by this treatment. This indicates that the $BrCl_2^{2-}$ is either a neutral center, just like the H center, or at most a negatively charged center with respect to the lattice.

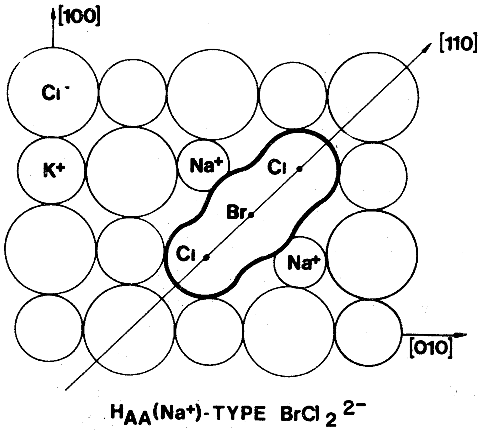
However, its very low concentration (even in the heavily Br^--doped samples) and its sample-dependent occurrence made it very unlikely that this $BrCl_2^{2-}$ represented the pure Br_i^0 center. It was therefore suspected that still another impurity was involved.

Because next to Br^-, Na^+ is the most common impurity in nominally pure KCl it was suspected that the latter impurity ion was involved. Therefore, KCl:Br^-:Na^+ crystals were investigated with various concentrations of Na^+ and Br^- impurities.

In KCl:Br^-:Na^+ crystals containing about 0.1 mol% of each impurity, it was found that a $BrCl_2^{2-}$ can be strongly observed after the following treatment. A few hours of x rays at 77 K yields a very weak $BrCl_2^{2-}$ ESR spectrum, plus rather strong spectra of the $H_A(Na^+)$,[7,8] $H_{AA}(Na^+)$, and $H_{A'A}(Na^+)$ centers,[10] the Cl_2^- V_K center[15,16] and the $BrCl^-$ and Br_2^- V_K-type centers.[16,17] An optical excitation of the F and F' centers wipes out the latter three centers very quickly, leaving the $H_A(Na^+)$, $H_{AA}(Na^+)$, $H_{A'A}(Na^+)Cl_2^-$ centers and the $BrCl_2^{2-}$



$H_A(Na^+)$-TYPE $BrCl_2^{2-}$
(a)



$H_{AA}(Na^+)$-TYPE $BrCl_2^{2-}$

FIG. 1. (a) Schematic model in a {100} plane of the $H_A(Na^+)$-type $BrCl_2^{2-}$ center in KCl. (b) Schematic model of the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ in KCl.

centers untouched. A subsequent warmup to 140 K for a few minutes destroys most of these *H*-type centers and at the same time the concentration of $BrCl_2^{2-}$ is strongly enhanced. Clearly, the mobile Cl_i^0 originating from the decaying *H*-type centers have been trapped to form $BrCl_2^{2-}$. This warmup to 140 K produces also a small amount of Cl_2^- V_K centers (because of the trapping of Cl_i^0 by α centers), but these are again quickly eliminated by a short optical excitation in the *F* band, either at 140 or 77 K. One is then left with an ESR spectrum showing a strong $BrCl_2^{2-}$ spectrum (plus another $BrCl_2^{2-}$ which will be discussed in Sec. VI). A further pulse anneal shows that this $BrCl_2^{2-}$ decays at 150 K. This center is called the $H_A(Na^+)$-type $BrCl_2^{2-}$ center and its model, as derived in Sec. V, is presented in Fig. 1(a). The thermal decay of this $H_A(Na^+)$-type $BrCl_2^{2-}$ results in the formation of yet another $BrCl_2^{2-}$ center possessing low symmetry and which is discussed in Sec. VI.

A second $KCl:Br^-:Na^+$ crystal was investigated in which both the Br^- and Na^+ concentrations were high (~1 mol%). Performing the same treatments on this crystal as described above, one finds that the thermal decay of the $H_A(Na^+)$-type $BrCl_2^{2-}$ at 150 K results in the formation of another strong $BrCl_2^{2-}$ ESR spectrum possessing high symmetry. Because this crystal has much higher Na^+ concentration, the probability that a Br^- impurity is associated with two Na^+ ions is appreciable. This center is therefore called the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ center and its model as derived in Sec. V is presented in Fig. 1(b): It is a perfectly linear molecule along [110] flanked by two Na^+ impurity ions along $[1\bar{1}0]$. The $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ center decays at 185 K, yielding, among other things, the low-symmetry $BrCl_2^{2-}$ center to be discussed in Sec. VI.

IV. ANALYSIS OF ESR SPECTRA

A. $H_{AA}(Na^+)$-type $BrCl_2^{2-}$

We shall start by describing the ESR spectra of the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ because it is the most symmetric one. The spectra are shown in Fig. 2 for three special directions of the static magnetic field $\vec{H}$. The main features of these spectra are readily recognized: four well-separated groups of lines with each group comprising two sets of seven dominant lines with intensity ratios 1:2:3:4:3:2:1. For the highest and the lowest group of lines, the two sets of seven lines are displaced with respect to one another by one hyperfine (hf) splitting resulting in an eight-line pattern.

The explanation of these hf patterns is straightforward. The four main "lines" originate from hf interaction with a Br nucleus. There are two equally abundant isotopes, namely, ^{79}Br and ^{81}Br, which have both nuclear spin-$\frac{3}{2}$ and somewhat different nuclear moments [$\mu_N(^{79}Br) = 2.0991$ and $\mu_N(^{81}Br) = 2.2626$ nuclear magnetons]. Thus there are two sets of four lines. Each of these four lines is split into seven lines with intensity ratios 1:2:3:4:3:2:1 because of hf interaction with two equivalent chlorine nuclei. Chlorine possesses two isotopes, namely, ^{35}Cl and ^{37}Cl, which are 75% and 25% abundant, respectively, and both with nuclear spin-$\frac{3}{2}$ and slightly different nuclear moments [$\mu_N(^{35}Cl) = 0.82091$ and $\mu_N(^{37}Cl) = 0.68330$ nuclear magnetons]. The seven dominant lines arise from interaction with two ^{35}Cl nuclei. Closer inspection of the experimental spectra shows that many of the ^{37}Cl isotope hf effects are resolved. The two Cl nuclei are, for this center, equivalent for all orientations of the static magnetic field $\vec{H}$, which indicates that we are dealing with a perfectly linear molecule in a ClBrCl configuration. That it is $BrCl_2^{2-}$ and not, e.g., $BrCl_2$ is indicated by the way the center is formed and by the analysis of the *g* and hf components which is presented in Sec. VII.

Analysis shows that the ESR spectra possess, to a first approximation, axial symmetry around $\vec{z} \parallel [110]$ for a given center. There is a small orthorhombic component to the $\vec{g}$ tensor (and probably also to the $\vec{A}$ tensor, but the precision of the analysis is not enough to resolve this) and the other two axes are $\vec{x} \parallel [001]$, $\vec{y} \parallel [1\bar{1}0]$.

B. $H_A(Na^+)$-type $BrCl_2^{2-}$

The $H_A(Na^+)$-type $BrCl_2^{2-}$ ESR spectra are not shown because they are in many respects identical to the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ ESR spectra presented in Fig. 1. It is clear that one is again dealing with a $\langle 110 \rangle$ oriented $BrCl_2^{2-}$ center in the symmetric $(ClBrCl)^{2-}$ configuration. There is one small but significant difference, however. The $\theta = 45°$ ESR spectrum obtained when $\vec{H} \parallel \langle 100 \rangle$ does not show the regular 1:2:3:4:3:2:1 chlorine hf pattern, but a pattern in which the degenerate components are split. This can be explained by accepting that the $BrCl_2^{2-}$ is, in this case, not a perfectly linear molecule but a bent one: the Br nucleus does not lie on the internuclear axis connecting the two Cl nuclei along [110], but is displaced from this axis in a $\{100\}$ plane. This has the result that the two Cl hf axes make angles $+\epsilon$ and $-\epsilon$ with $\vec{z} \parallel \langle 110 \rangle$ which is the Cl-Cl direction. Thus this $BrCl_2^{2-}$ has C_{2v} symmetry, suggesting the presence of a perturbing impurity next to the Br in the $\{100\}$ plane.

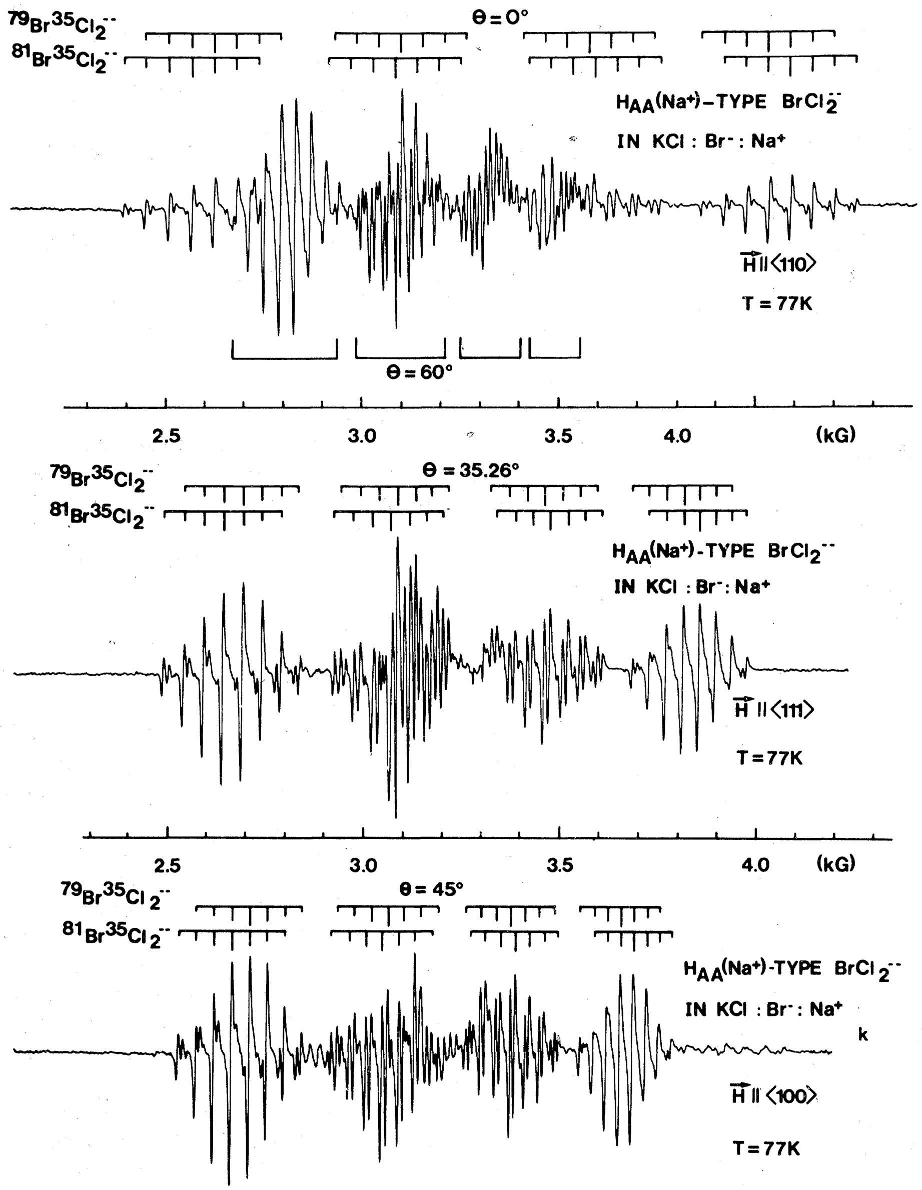


FIG. 2. ESR spectra of the $H_{AA}(\mathrm{Na}^+)$-type $\mathrm{BrCl_2}^{2-}$ center in KCl for three special orientations of the static magnetic field $\vec{H}$. The microwave frequency is 9.240 GHz.

C. Quantitative analysis

The $\mathrm{BrCl_2}^{2-}$ ESR spectra were fitted to the following spin-Hamiltonian (in the usual notation):

$$\frac{\mathcal{H}}{g_0\mu_B}=\frac{1}{g_0}\,\vec{H}\cdot\vec{g}\cdot\vec{S}+\vec{S}\cdot\vec{A}(\mathrm{Br})\cdot\vec{I}(\mathrm{Br})+\sum_{i=1}^{2}\vec{S}\cdot\vec{A}_i(\mathrm{Cl})\cdot\vec{I}_i(\mathrm{Cl})+P(\mathrm{Br})I_z^2(\mathrm{Br}),\quad(1)$$

in which the various hf tensor axes may, or may not, coincide with each other and with the g-tensor axis depending on the center. For the two $\mathrm{BrCl_2}^{2-}$ centers which we have discussed so far one has $|\vec{A}_1(\mathrm{Cl})|=|\vec{A}_2(\mathrm{Cl})|$. The Cl quadrupole effects are too small to be detected.

The fitting of (1) to the experimental data was done using a perturbation solution (a combination of those given in Refs. 12 and 18) and the results are summarized in Table I, together with the H-center data in KCl,[10] and KBr.[1] A discussion of these parameters is given in Sec. VII.

D. $\mathrm{ICl_2}^{2-}$ centers

The $H_A(\mathrm{Na}^+)$-type and $H_{AA}(\mathrm{Na}^+)$-type $\mathrm{ICl_2}^{2-}$ centers have been observed in KCl doped with suitable concentrations of both Na⁺ and I⁻. The production of these centers parallels those of the $\mathrm{BrCl_2}^{2-}$ centers; their thermal stability is somewhat higher

TABLE I. Spin-Hamiltonian parameters of the three $BrCl_2^{2-}$ centers in KCl. The hyperfine parameters are given in G and correspond to the ^{81}Br and ^{35}Cl nuclei. For comparison the H-center data in KCl and KBr are included. T_{decay} is given in K, and ΔH (in G) is the linewidth between the extrema of the first derivative.

Center	g_z	g_x	g_y	A_z(Br)	$A_\perp$(Br)	A_z(Cl)	$A_\perp$(Cl)	P(Br)	P(Cl)	ΔH	T_{decay}
$H_A(Na^+)$-type $BrCl_2^{2-}$[a,b]	1.9889 ± 0.0003	2.082 ± 0.004	2.106 ± 0.007	+501.3 ± 0.2	(±)35 ± 20	+55.5 ± 0.5	+16 ± 5	···	···	4.9 ± 0.5	150
$H_{AA}(Na^+)$-type $BrCl_2^{2-}$[a]	1.9893 ± 0.0003	2.076 ± 0.003	2.104 ± 0.006	+502.1 ± 0.2	(±)41 ± 12	+56.2 ± 0.5	+16 ± 1	+28 ± 4	···	5.0 ± 0.5	185
Diinterstitial $BrCl_2^{2-}$[c]	1.9886 ± 0.0003	2.120 ± 0.006	2.076 ± 0.006	+502.5 ± 1	(±)50 ± 25	{+62.5 ± 1 +49.0 ± 1	{+15 ± 15 +15 ± 15	···	···	6.0 ± 0.5	210
H center Cl_2^- in KCl[a]	2.0018 ± 0.0002	2.0221 ± 0.0005	2.0227 ± 0.0005			+108.6 ± 0.1	+16 ± 1.5		−5 ± 2	1.2 ± 0.1	40
H center Br_2^- in KBr[a]	1.993 ± 0.001	2.070 ± 0.005	2.078 ± 0.005	+498 ± 1	+59.5 ± 5			···		2.5 ± 0.5	

[a] For the H-, H_A-, and H_{AA}-type centers, $\vec{z} \parallel [110]$, $\vec{x} \parallel [001]$, $\vec{y} \parallel [1\bar{1}0]$.

[b] The $H_A(Na^+)$-type $BrCl_2^{2-}$ molecule is bent by 14° ± 5° [see Fig. 1(a)], assuming that the two Br-Cl bonds are not bent.

[c] For the di-interstitial $BrCl_2^{2-}$, $\vec{z} \parallel [\langle 100\rangle + 22°$ in $\{110\}]$, $\vec{x} \parallel [001]$.

than the corresponding $BrCl_2^{2-}$. Figure 3 gives an example of the $H_{AA}(Na^+)$-type ESR spectrum. The six main "lines" originate from the hf interaction with the 100% abundant ^{127}I nucleus which has nuclear spin-$\frac{5}{2}$. The spin-Hamiltonian parameters are given in Table II. For the $H_A(Na^+)$-type ICl_2^{2-} only the $\theta = 0°$ was analyzed. As a result g_x, g_y, $A_\perp$(Cl), and the bending angle could not be determined. The quadrupole parameter P(I) could not be reliably determined with the perturbation formulas that were employed. The conclusions regarding the electronic structure of the $BrCl_2^{2-}$ as given in Sec. VII also hold for the ICl_2^{2-}.

Finally, it should be mentioned that if the I^--doped KCl crystals were grown in air, one produces quite strongly after x or γ irradiation at 77 K an IOH^- interstitial-type center[19,4] which is very similar to the ⟨111⟩ oriented FI^- center[12,13] in KCl. No analogous $BrOH^-$ was observed at 77 K in KCl, but it has been observed at this temperature in NaCl.[4]

V. MODELS OF THE $H_A(Na^+)$- AND $H_{AA}(Na^+)$-TYPE $BrCl_2^{2-}$ CENTERS

The experimental facts from which the $H_A(Na^+)$-type $BrCl_2^{2-}$ center model is to be derived can be summarized as follows: (i) it is a symmetric molecule of the type $(ClBrCl)^{2-}$; (ii) the molecule is bent by about 14° in a {100} plane; (iii) it is a ⟨110⟩ oriented center; (iv) it is either a neutral or a negatively charged center with respect to the lattice; (v) it occurs in KCl crystals containing small (i.e., ~0.1 mol%) of both Na^+ and Br^- ions, and not in KCl containing only Br^-; and (vi) its intensity increases where the $H_A(Na^+)$ centers decay at 120 K indicating that it is formed by trapping of a mobile Cl_i^0 center (H center).

The model of the $H_A(Na^+)$-type $BrCl_2^{2-}$ center as depicted in Fig. 1(a) agrees with all these observations. In particular, the center is electrically neutral and the bending of the molecule is induced by the presence of the Na^+ impurity on one side of the $BrCl_2^{2-}$ and immediately adjoining the Br. There is little doubt that this $H_A(Na^+)$-type $BrCl_2^{2-}$ is formed when a mobile Cl_i^0 is trapped by a pair of substitutional Na^+ and Br^- impurity ions which are nearest neighbors of one another. This center may be thought of as representing the Br_i^0 center in KCl stabilized by a Na^+ impurity ion.

Most of the experimental facts underlying the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ center model are the same as for the $H_A(Na^+)$-type model given above, except for two important differences: (a) one needs a higher Na^+ concentration (~1 mol%) suggesting that *two* Na^+ ions, rather than one, are involved; and (b) the $BrCl_2^{2-}$ molecule is perfectly linear.

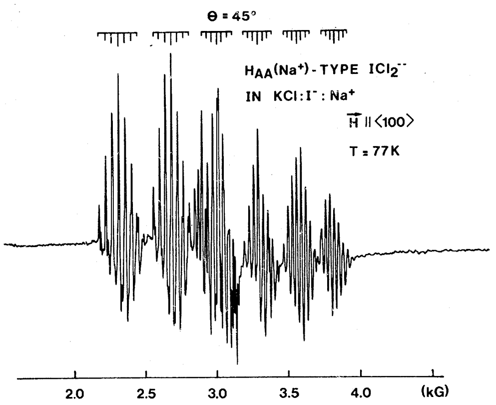


FIG. 3. Example of an ICl_2^{2-} ESR spectrum: The H_{AA}(Na$^+$)-type ICl_2^{2-} in KCl for $\vec{H}$ ∥ ⟨100⟩. The microwave frequency is 9.240 GHz.

The model agreeing with all these facts is shown in Fig. 1(b), and it is clear that this center may be described as being an H_{AA}(Na$^+$)-type $BrCl_2^{2-}$ center. This center is thought to be formed when a mobile Cl_i^0 is trapped by a triangular complex of nearest-neighbor ions: two substitutional Na$^+$ ions and one substitutional Br$^-$. This center represents the Br_i^0 center in KCl stabilized by two Na$^+$ impurity ions.

Whether or not preferential association of Br$^-$ and Na$^+$ contributes to the concentration of the two foregoing centers is a question that will require detailed quantitative study.

Because all hole and interstitial centers analyzed so far in the alkali halides always manifest themselves as *diatomic* homonuclear or heteronuclear halogen molecule ions,[4,5] one may wonder whether or not we are seeing in both cases motionally averaged ESR spectra at 77 K. In other words, it is possible *a priori* that these centers are really BrCl$^-$ molecule ions on a single negative ion site (next to the one or the two Na$^+$ ions) and that at 77 K the Br jumps back and forth between the two positions along ⟨110⟩ which are equivalent with respect to the Na$^+$ impurity ions. Such a motion would be identical to the restricted interstitial motion of the H_A(Na$^+$) center in KCl.[7,20]

However, such a motion does not exist for these $BrCl_2^{2-}$ centers. The ESR spectra observed at 4.2 K are identical to the ones at 77 K, indicating that the Br does not relax to an asymmetric position. In other words, the Br does, at all temperatures, occupy the symmetric interstitial position as indicated in Figs. 1(a) and 1(b), and one is dealing with a genuine triatomic molecule ion. This ESR experiment at 4.2 K also showed that the $BrCl_2^{2-}$ lines saturate very strongly indicating a rather long spin-lattice relaxation time.

Many interstitial centers in the alkali halides possess several distinct reorientation motions oftentimes characterized by activation energies low enough to result in motionally averaged ESR spectra, or at least in strongly broadened lines, at 77 K.[4,6,7,10,14,20] Inspection of the H_A(Na$^+$)-type $BrCl_2^{2-}$ model in Fig. 1(a) shows that the interstitial bromine can have 12 equivalent positions around a Na$^+$ impurity. Whether or not the Br jumps among these 12 positions (in some type of pyramidal motion) above some temperature is not yet clear. No line-broadening effects caused by rapid motions were observable at 77 K in the ESR spectra. Optical anisotropy experiments are able to establish the existence of slow motions[4] and

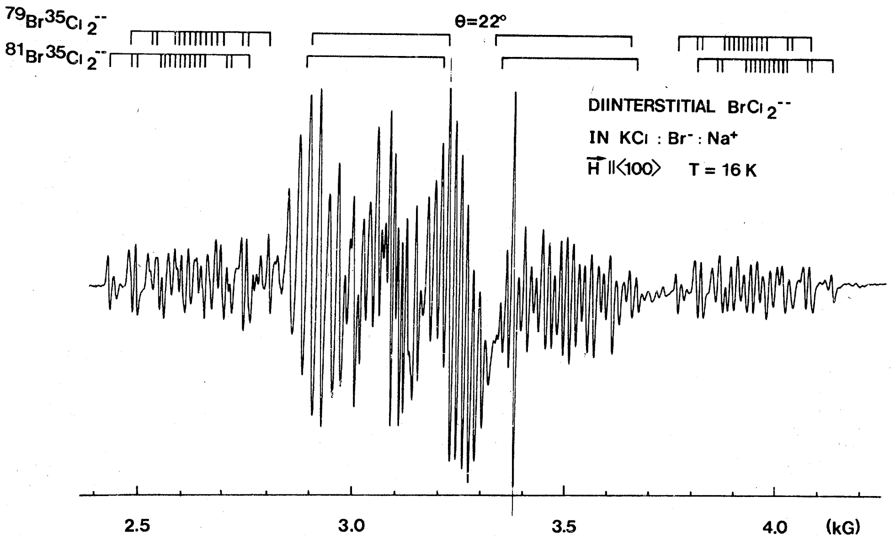


FIG. 4. ESR spectrum of the di-interstitial $BrCl_2^{2-}$ center in KCl for $\vec{H}$ ∥ ⟨100⟩. The microwave frequency is 9.240 GHz.

TABLE II. Spin-Hamiltonian parameters of the ICl_2^{2-} centers in KCl. The hyperfine parameters (in G) correspond to the ^{127}I and ^{35}Cl nuclei. The linewidth (in G) is between the extrema of the first derivative. T_{decay} is given in K. For comparison the results for the I_2^- V_K center in KI are included.

Center	g_z [110]	g_x [001]	g_y [$1\bar{1}0$]	A_z(I)	$A_\perp$(I)	A_z(Cl)	$A_\perp$(Cl)	ΔH	T_{decay}
$H_A(Na^+)$-type ICl_2^{2-}	1.9256 ±0.0005	...	...	+450 ±4	+50 ±20	+52 ±1	...	6 ±1	185
$H_{AA}(Na^+)$-type ICl_2^{2-}	1.9412 ±0.0005	2.131 ±0.005	2.198 ±0.005	+466 ±1	+46 ±20	+55.1 ±0.5	+21 ±2	6 ±1	240
I_2^- V_K center in KI[a]	1.9037 ±0.0005	(2.29)	2.266 ±0.021	+384.8 ±0.1	+140 ±5			11.0 ±1	105

[a] From Ref. 16; the I_2^- quadrupole parameter is $P(I) = +33.2$ G.

should be employed in such an investigation.

The structure of the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ as depicted in Fig. 1(b) implies that it is a rigid center, i.e., it cannot have reorientation motions. It shares this property with the H_{AA} centers[10] and the V_{KAA} centers.[16]

VI. DI-INTERSTITIAL $BrCl_2^{2-}$ CENTER

In the KCl samples containing both the Na^+ and Br^- ions in the low concentration one can observe yet another strong $BrCl_2^{2-}$ ESR spectrum. It is not detected immediately after x irradiation at 77 K but is formed after a warmup to about 110 K which is the decay temperature of the $H_A(Na^+)$ Cl_2^- center.[7,10] It increases further when the $H_A(Na^+)$-type $BrCl_2^{2-}$ decays thermally at 150 K. The spectrum for $\vec{H} \parallel \langle 100 \rangle$ is shown in Fig. 4 and comparison with Fig. 2 leaves no doubt that this ESR spectrum too originates from a $BrCl_2^{2-}$ molecule ion. However, the lines are somewhat broader and the hf interaction with the two Cl nuclei does not exhibit the 1:2:3:4:3:2:1 intensity distribution; rather, 16 lines of equal intensity are observed. Furthermore, angular variation studies in the $\{100\}$ and $\{110\}$ planes show that this $BrCl_2^{2-}$ does not lie along $\langle 110 \rangle$, but that it lies in a $\{110\}$ plane where its internuclear axis makes a 22° angle with $\langle 100 \rangle$. A quantitative analysis shows that the two Cl nuclei are inequivalent (by about 20%) and that their hf axes probably do not coincide with each other or with the Br hf axis, although it is difficult to get a good quantitative determination of this with a perturbation solution of the spin Hamiltonian. We will further consider this center to be linear.

The spin-Hamiltonian parameters are listed in Table I. It is seen that the g and hf values are quite close to those of the $H_A(Na^+)$- and $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ centers.

That this center is either neutral or negatively charged with respect to the lattice is proven by the fact that optical excitation of the F centers with an intense beam of light does hardly affect the concentration of this $BrCl_2^{2-}$. Thus the freed electrons are not attracted, or may be even repelled, by this center. This experiment gives an indication that this $BrCl_2^{2-}$ too is some type of an interstitial center.

However, we know already the structure of Br_i^0 centers stabilized by one or two Na^+ ions: they are the $H_A(Na^+)$-type and the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ centers. Furthermore, because this new $BrCl_2^{2-}$ is produced in crystals possessing a low Na^+ concentration it is not reasonable to propose a $BrCl_2^{2-}$ model with, say, three Na^+ ions in the immediate neighborhood. In fact, whatever the model, it is likely that only *one* Na^+ ion is involved.

One could then entertain the idea that, at sufficiently low temperatures, a Br_i^0 can be trapped in the immediate vicinity of a Na^+ in *two* different but stable configurations, one being the ⟨110⟩ oriented $H_A(Na^+)$-type $BrCl_2^{2-}$ already established. After all, interstitial centers stabilized in a low-symmetry configuration by a single alkali-impurity ion have been observed, such as the $H_A(Li^+)$-type Cl_2^-,[9,20] $BrCl^-$, and ICl^- centers.[14] The molecular axes of these centers too lie in a {110} plane.[21] However, if one tries to propose a model along the $H_A(Li^+)$-type $BrCl^-$ center model, one runs into the serious difficulty of making reasonable the fact that the center involves, besides the Br, two Cl nuclei which are not all that much inequivalent.

The impossibility of finding a reasonable $BrCl_2^{2-}$ model involving a single interstitial next to a Na^+ and agreeing with the observed ESR symmetry leads one to propose the di-interstitial $BrCl_2^{2-}$ model as shown in Fig. 5. In this model, the $BrCl_2^{2-}$ occupies a *single* negative ion site next to a substitutional Na^+. In other words, the proposed model involves two interstitial halogens. Thus this center is thought to be formed by the trapping of both an interstitial Cl_i^0 atom and an interstitial Cl_i^- ion by a pair of substitutional Na^+ and Br^- ions which occupy nearest-neighbor sites to one another. The model shown in Fig. 5 is the simplest and most reasonable one which is in agreement with the experimental facts. Note in particular that, (i) the center is negatively charged with respect to the lattice, (ii) the model clearly involves two inequivalent Cl nuclei, and (iii) the low-symmetry configuration is likely to induce bending of the molecule and the two molecular bonds.

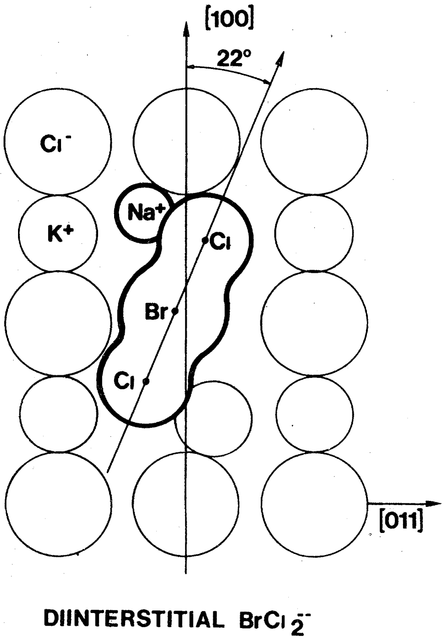


FIG. 5. Schematic model in a {110} plane of the di-interstitial $BrCl_2^{2-}$ center in KCl.

The di-interstitial $BrCl_2^{2-}$ decays at 210 K which is about 20 K higher than the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$. The decay mechanism has not been investigated. Quite possibly one or both interstitial chlorines break away from the center. The decay is certainly not caused by recombination with V_K centers, whose decay temperature happens to be near 210 K,[16] because the V_K centers were always bleached out optically at 77 K in our experiments by an optical excitation of *F* centers.

Inspection of the diinterstitial $BrCl_2^{2-}$ model in Fig. 5 indicates that, in principle, a pyramidal motion[4,20] of C_{4v} symmetry around [001] among the four equivalent orientations in {110} planes, could exist. However, no linebroadening caused by a rapid motion is present at 77 K, leaving at most a slow motion at this temperature.

Finally, a di-interstitial model very similar to the one given here has been proposed by Plant for a F_3^{2-} center next to a Li^+ impurity ion in NaF:Li^+.[22]

VII. $BrCl_2^{2-}$ ELECTRONIC STRUCTURE

Considering that the $BrCl_2^{2-}$ centers are formed by trapping of one or two interstitial halogens, the valency of the center as a $BrCl_2^{2-}$ rather than a $BrCl_2$ seems by far the most likely one. The discussion of the *g* and hf values to be given below agrees with this valency. The three halogens contribute a total of 17 *p* electrons to the molecular bonds, and because the molecule is expected to be linear[23] they are accomodated in the following configuration:

$$(\sigma_{u,b})^2(\pi_{u,b})^4(\sigma_g)^2(\pi_g)^4(\pi_{u,a})^4(\sigma_{u,a})^1 , \qquad (2)$$

where *a* and *b* stand for antibonding and bonding, respectively. The gerade orbitals are probably nonbonding or weakly bonding. The ordering of the orbitals in (2) is based on this bonding character and is probably essentially correct. This orbital scheme together with pictorial expressions for the molecular orbitals is shown in Fig. 6. For the gerade orbitals one can have only *s* or *d* functions on the bromine.

According to (2), the unpaired electron is in a σ_u orbital giving a $^2\Sigma_u^+$ ground state for the $BrCl_2^{2-}$ molecule. This is the same type of ground state as in the case of the diatomic halogen centers, such as the homonuclear V_K or *H* centers or the heteronuclear V_K-type (BrCl, ICl^-, etc.) and *H*-type (FCl^-, . . .) centers. The qualitative behavior of the $BrCl_2^{2-}$ ESR spectra should therefore be similar to those of the diatomic halogen centers. In particular one should observe (i) maximum hf

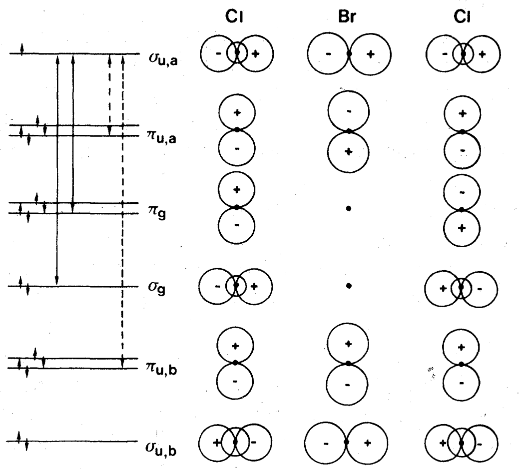


FIG. 6. Schematic orbital level scheme of the $BrCl_2^{2-}$ molecule ion. The solid vertical lines indicate allowed optical transitions; the broken vertical lines connect orbitals mixed by spin-orbit coupling. For the gerade orbitals only *s* and/or *d* orbitals can be on the bromine.

separation along the molecular axis and minimum hf separation perpendicular to it, (ii) a negative g_z shift $\Delta g_z = g_z - g_0$ which is second order, and (iii) positive g_x and g_y shifts which are predominantly first order. Inspection of Table I, where the comparison with the diatomic *H* centers can be made, indeed shows that the $BrCl_2^{2-}$ spin-Hamiltonian parameters have the expected behavior for a $^2\Sigma_u^+$ state.

Within the framework of configuration (2) is it straightforward to calculate expressions for the *g* and hf components of $BrCl_2^{2-}$. We note that on symmetry grounds spin-orbit coupling will only mix $\pi_{u,a}$ and $\pi_{u,b}$ into $\sigma_{u,a}$ and this will result in two positive first-order contributions to g_x and g_y (in the free $BrCl_2^{2-}$ molecule $g_x \equiv g_y$, but in a site of D_{2h} symmetry or lower, the orbital degeneracy of π_u is lifted giving $g_x \neq g_y$). The structure of the expressions for the *g* components will be *formally* identical to the ones derived for the heteronuclear XY^- centers.[12] Because these expressions contain too many unknown molecular parameters they are not very useful at this point, and therefore these results are not reproduced here.

Similarly, in order to do an accurate analysis of the $BrCl_2^{2-}$ hf data, one has to include higher-order corrections similar to the ones employed in the analysis of the V_K-center hf data.[16] Again these expressions will contain too many unknown molecular parameters.

It is clear that an accurate analysis of the ESR data will require a considerable numerical effort. As an alternative to this we will present an approximate quantitative analysis of the hf data which will permit at least a qualitative insight into the distribution of the unpaired hole throughout the $BrCl_2^{2-}$ molecule. To this end we remark that if we apply the following well-known zero-order expressions for the hf components:

$$A_\parallel = A + 2\rho, \quad A_\perp = A - \rho \tag{3}$$

to the Cl_2^- V_K-center data, that we obtain a value for the isotropic part $A(\mathrm{Cl})$ which is about 8% too high compared to the more accurate value, and a value for the anisotropic part $\rho(\mathrm{Cl})$ which is about 8% too low.[16] For the Br_2^- V_K center, these percentages are, respectively, 38% and 30%. For the Cl_2^- and Br_2^- *H* centers the perpendicular *g* shifts $\Delta g_\perp = g_\perp - g_0$ are just about half the size of the corresponding V_K-center shifts, and because the hf correction terms are to first order a linear function of $\Delta g_\perp$,[16] this will roughly halve the corrections. Therefore, because the corrections for the Cl_2^- and Br_2^- *H* centers and the *H*-type $BrCl_2^{2-}$ centers are expected to be roughly comparable, the *H* center and $H_{AA}(\mathrm{Na}^+)$-type $BrCl_2^{2-}$ ESR data of Table I were analyzed using formulas (3) followed by an increase of the $\rho(\mathrm{Cl})$ and $\rho(\mathrm{Br})$ values by 4% and 15%, respectively, and by a decrease of the $A(\mathrm{Cl})$ and $A(\mathrm{Br})$ values by 4% and 19%, respectively. In doing the analysis it was assumed that the $A_\perp(\mathrm{Br})$ and $A_\perp(\mathrm{Cl})$ values of the Br_2^- and Cl_2^- *H* centers have a positive sign. (There can be no doubt that all A_z values are positive.[16]) This is a reasonable assumption because the positive sign of $A_\perp$ for the Cl_2^- and Br_2^- V_K centers is well established[16] and because the hyperfine parameters of the V_K and *H* centers are quite comparable. Comparing in Table I the bromine hf values of $BrCl_2^{2-}$ with those of the Br_2^- *H* center, it seems likely that here too $A_\perp(\mathrm{Br})$ is positive. However, we note that $|A_\perp(\mathrm{Br})| \ll |A_z(\mathrm{Br})|$ and so for our rough analysis the actual sign of $A_\perp(\mathrm{Br})$ will not be of decisive quantitative significance. The sign of $A_\perp(\mathrm{Cl})$ is quite important but not readily guessed. Thus the results of the $BrCl_2^{2-}$ analysis as presented in Table III are given for both signs of $A_\perp(\mathrm{Br})$ and

TABLE III. Anisotropic part ρ and the isotropic part A (both in G) of the hyperfine interaction for the Cl_2^- *H* center in KCl, the Br_2^- *H* center in KBr and the $H_{AA}(\mathrm{Na}^+)$-type $BrCl_2^{2-}$ center in KCl.

Center	$\rho(\mathrm{Br})$	$A(\mathrm{Br})$	$\rho(\mathrm{Cl})$	$A(\mathrm{Cl})$
Cl_2^- *H* center			32.2	45.4
Br_2^- *H* center	178	177		
$BrCl_2^{2-}$ $H_{AA}(\mathrm{Na}^+)$-type	181^a 208^b	158^a 113^b	14.0^a 25^b	28.2^a 8.5^b

[a] Taking $A_\perp$ positive. [b] Taking $A_\perp$ negative.

$A_{\perp}(\mathrm{Cl})$. Considering the experimental errors on the hf components and the approximate nature of the analysis, these values should be approached with some caution.

In order to discuss the results of Table III it should be realized that ρ, rather than A, is the measure for the population of the unpaired hole on a constituent atom.[16] The isotropic part A is the sum of various contributions such as s mixing, core polarization, configuration interaction, and relativistic effects. Their contribution to the observed hf separation can be large but their presence relates only to a small percentage of the total wave function.

Compared to the Br_2^- H center, $\rho(\mathrm{Br})$ or BrCl_2^{2-} has either remained about the same [if $A_{\perp}(\mathrm{Br}) > 0$ holds] or increased by about 15% [if $A_{\perp}(\mathrm{Br}) < 0$ holds]. Comparing $2\rho(\mathrm{Cl})$ or BrCl_2^{2-} with $\rho(\mathrm{Cl})$ of the H center, the former is smaller by 10% to 15% than the latter if $A_{\perp}(\mathrm{Cl}) > 0$ is taken, but it is very much larger (~50%) if $A_{\perp}(\mathrm{Cl}) < 0$. The latter situation is very unlikely if only because the electronegativity of Br is a little bit smaller than the one of Cl,[24] and one can accept a small increase of the unpaired hole density on the bromine much more readily than a strong increase of it on the two chlorines. Thus, we reject the $A_{\perp}(\mathrm{Cl}) < 0$ possibility, but the situation for $A_{\perp}(\mathrm{Br})$ is less clear cut. However, our rough analysis allows us to say quite safely that half, or a little more than half, of the unpaired hole density resides on the Br in BrCl_2^{2-}, while the remaining half is shared equally by the two chlorines. This conclusion also holds for the $H_A(\mathrm{Na}^+)$-type BrCl_2^{2-}. In the case of the di-interstitial BrCl_2^{2-} it is clear that again one-half of the unpaired hole density resides on the Br, but than one Cl constituent has a bit more of the unpaired hole than the other. However, the error on $A_{\perp}(\mathrm{Cl})$ makes a further quantitative estimate of this shift between the chlorines rather meaningless.

Turning to the isotropic part we see that when $2A(\mathrm{Cl})$ of BrCl_2^{2-} is compared to $A(\mathrm{Cl})$ of the Cl_2^- H center, that the former is a bit larger than the latter. This can be formally accounted for by saying that, apart from the factor 2, the s character of the s-p hybrids on each Cl in BrCl_2^{2-} is larger than the s character of the s-p hybrids on the chlorines in the Cl_2^- H center.

Comparing $A(\mathrm{Br})$ of BrCl_2^{2-} with $A(\mathrm{Br})$ of the Br_2^- H center one notes a distinct decrease of the former whatever sign for $A_{\perp}(\mathrm{Br})$ one chooses. In trying to explain this $A(\mathrm{Br})$ of BrCl_2^{2-} one runs into something of a surprise. Indeed, on each Br of the Br_2^- H center an s-p hybrid is allowed by symmetry into the $^2\Sigma_u^+$ ground state, whereas for the $^2\Sigma_u^+$ ground state of BrCl_2^{2-} no s mixing is allowed on the Br (Fig. 6). The presence of isotropic hf interaction on the Br in BrCl_2^{2-} is in itself not surprising because configuration interaction and/or exchange polarization may account for it. What is maybe surprising is the size of the $A(\mathrm{Br})$ values of BrCl_2^{2-} for both choices of the sign of $A_{\perp}(\mathrm{Br})$. They are comparable to the $A(\mathrm{Br})$ value of the Br_2^- H center. Only accurate molecular calculations can shed light on this.

Finally, configuration (2) suggests that BrCl_2^{2-} should possess two optical absorption bands originating from excitations $\pi_g \rightarrow \sigma_{u,a}$ and $\sigma_g \rightarrow \sigma_{u,a}$. Inspection of the matrix elements of the electric dipole operator suggests that the last transition is a strong one. A preliminary optical absorption experiment on the $H_{AA}(\mathrm{Na}^+)$-type BrCl_2^{2-} has yielded a strong absorption band around 380 nm which we ascribe to the $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transition. There is also experimental evidence for a weaker transition at ~580 nm on the low-energy tail of the F band. This latter transition is ascribed to the $^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transition which is expected to be weak. Thus the order of the σ_g and π_g orbitals as presented in (2) is very likely correct.

ACKNOWLEDGMENTS

A NATO Research Grant, support from the Belgian science supporting agencies NFWO and IIKW, and discussions with P. H. Yuster and C. T. Delbecq are gratefully acknowledged.

---

†Work performed in part under the auspices of the U.S. Energy Research and Development Administration.

*Permanent address.

[1] W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 70 (1958).

[2] C. J. Delbecq, J. L. Kolopus, E. L. Yasaitis, and P. H. Yuster, Phys. Rev. 154, 866 (1967).

[3] Y. H. Chu and R. L. Mieher, Phys. Rev. 118, 1311 (1969).

[4] For recent surveys covering the magnetic resonance and structure of H-type centers, see D. Schoemaker, in *Defects and their Structure in Nonmetallic Solids*, edited by B. Henderson and A. E. Hughes (Plenum, New York, 1976); D. Schoemaker, J. Phys. (Paris) Colloque 37, 7C7-63 (1976).

[5] Review papers covering extensively the properties of hole and interstitial centers in ionic crystals are M. N. Kabler, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972); N. Itoh, Crystal Lattice Defects 3, 115 (1972).

[6] K. Bachmann and W. Kanzig, Phys. Kondens. Materie 7, 284 (1968).

[7] C. J. Delbecq, E. Hutchinson, D. Schoemaker, E. L. Yasaitis, and P. H. Yuster, Phys. Rev. 187, 1103 (1969).

[8] F. W. Patten and F. J. Keller, Phys. Rev. 187, 1120 (1969).

[9] D. Schoemaker and J. L. Kolopus, Phys. Rev. B 2, 1148 (1970).

[10] D. Schoemaker, Phys. Rev. B 3, 3516 (1971).

[11] J. W. Wilkins and J. R. Gabriel, Phys. Rev. 132, 1950 (1960).

[12] D. Schoemaker, Phys. Rev. 149, 693 (1966).

[13] W. Dreybrodt, Phys. Status Solidi 21, 99 (1967).

[14] D. Schoemaker and C. T. Shirkey, Phys. Rev. B 6, 1562 (1972).

[15] T. G. Castner and W. Kanzig, J. Phys. Chem. Solids 3, 178 (1957).

[16] D. Schoemaker, Phys. Rev. B 7, 786 (1973); A. Lagendijk and D. Schoemaker, *ibid.* 11, 4030 (1975).

[17] C. J. Delbecq, D. Schoemaker, and P. H. Yuster, Phys. Rev. B 3, 473 (1971); 7, 3933 (1973); 9, 1913 (1974).

[18] D. Schoemaker, Phys. Rev. 174, 1060 (1968).

[19] D. Schoemaker and F. Waldner, Helv. Phys. Acta 44, 560 (1971).

[20] D. Schoemaker and E. L. Yasaitis, Phys. Rev. B 5, 4970 (1972).

[21] This statement has to be qualified somewhat for the $H_A(Li^+)$ center in KCl:Li$^+$. A recent careful analysis of the ESR data with and without uniaxial stress has shown that for the $H_A(Li^+)$ center in KCl:Li$^+$ the Cl_2^- librates fast over a large angle with respect to a $\{110\}$ plane. One can only say that the *average* Cl_2^- orientation is a $\{110\}$ plane; see D. Schoemaker and A. Lagendijk, Phys. Rev. B 15, 115 (1977).

[22] W. Plant, Solid State Commun. 11, 1219 (1972).

[23] R. J. Buenker and S. D. Peyerimhoff, Chem. Rev. 74, 127 (1974).

[24] G. Klopman, J. Chem. Phys. 43, 124 (1965).