PHYSICAL REVIEW B VOLUME 23, NUMBER 4 15 FEBRUARY 1981

Electron-spin-resonance study of complex interstitial halogen H_D-type defects in KCl doped with divalent cations

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(Received 15 July 1980)

An extensive electron-spin-resonance study has been made of trapped interstitial halogen defects in KCl doped with divalent cations ($M^{2+} = Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}$, or Sn^{2+}). It is shown that x-irradiation-produced interstitial halogens can be trapped by monomers and dimers of M^{2+}, positive-ion vacancy complexes. These defects, which manifest themselves as Cl_2^- or Cl_3^{2-} species, are called H_D-type centers and altogether five different centers have been detected and studied. One is a di-interstitial halogen defect associated with an M^{2+}-vacancy monomer. Two other defects involve dimers of M^{2+}-vacancy complexes in configurations possessing inversion symmetry. The last two defects involve a Cl_2^- associated with a monomer complex in which the M^{2+} is either nearest neighbor or next-nearest neighbor to the positive-ion vacancy. A careful analysis of the electron-spin-resonance spectra reveals that in both these centers the Cl_2^- molecule performs a librational motion with respect to the symmetry plane of the defect.

I. INTRODUCTION

The fundamental point defects in simple solids (the ionic alkali and alkaline-earth halides, elemental semiconductors, monoatomic metals, simple oxides) are by now very well characterized. These defects are obtained by doping (atomic or small molecular impurities), by ionizing or neutron irradiation (mostly at low temperatures), or by mechanical, thermal and chemical treatments. Studies in defect physics evolve toward the study of more complex aggregates of defects in solids.

This paper is concerned with an electron-spin-resonance (ESR) study of a series of complex interstitial halogen defects produced by x irradiation at 77 K in alkali halides doped with small amounts of divalent cations, M^{2+}.

The structure and properties of the fundamental interstitial halogen defects in the alkali halides are well established: The interstitial halogen atom known as the H center,[1-3] and the interstitial halogen negative ion known as the I center,[4] have been studied in great detail. Furthermore the stabilization of interstitial halogens by monovalent alkali and halogen impurities[5] and the interaction between interstitial halogens leading to di-interstitial centers,[4,6,7] have also been extensively investigated.

The effect of divalent cations, M^{2+}, and their associated charge-compensating positive-ion vacancies, (+), on the physical properties of alkali halides has also been a field of fruitful studies for quite a long time. Prominent investigations include the influence on the ionic conductivity[8] and on the dielectric properties,[9] the aggregations of $[M^{2+}, (+)]$ complexes,[10] the Suzuki phase in particular,[11] the electron- and hole-trapping properties of some of these ions,[12-16] the association of $[M^{2+}, (+)]$ complexes with F-center-like defects leading to the so-called Z centers,[17] etc.

An exploratory ESR and optical absorption investigation on x-irradiated KCl and KBr doped with Ba^{2+}, Ca^{2+}, and Sr^{2+} was carried out some time ago by Hayes and Nichols.[18] Their ESR analysis, though rather inaccurate, established the presence of radiation-produced Cl_2^- and Br_2^- molecules in the neighborhood of single $[M^{2+}, (+)]$ complexes. The spectra were at first interpreted as originating from X_2^- hole centers (V_K centers)[19] stabilized by one $[M^{2+}, (+)]$ complex, but subsequent optical studies established that interstitial halogens were involved.[20] Further ESR work has underscored the complexity of the defects.[21]

The present paper confirms the interstitial and di-interstitial character of these defects. It will be shown that, just like monovalent impurities,[5] monomers and dimers of $[M^{2+}, (+)]$ complexes can stabilize radiation-produced mobile interstitial halogens in several distinct configurations. A total of five different ESR spectra have been identified and analyzed.[22] It proved possible to present convincing models for these complex defects and to detect the presence of librational motions in some of them. Considering the complexity and volume of the subject, the experiments were limited to employing the ESR technique. No serious effort was made to correlate, e.g., the ESR results to the optical absorption data although such an investigation could be a very interesting one.

II. EXPERIMENTAL

The doped KCl crystals used in these experiments were grown either by the Kyropoulos or the Bridgman method. To the KCl melt, roughly 0.05 to 0.5 mol % of the appropriate MCl_2 was added.

$$\alpha = a^2 + \tfrac{1}{2}b^2 + 2ab(\sin\psi_b'' - \sin\psi_a'')/\Delta\psi'' + \tfrac{1}{4}b^2(\sin 2\psi_b'' - \sin 2\psi_a'')/\Delta\psi'' , \tag{7}$$

$$\beta = \frac{ac}{b} + c(\sin\psi_b'' - \sin\psi_a'')/\Delta\psi'' - \frac{a}{c}\alpha ,$$

which yields

$$\beta = ad(\sin\psi_b'' - \sin\psi_a'')/\Delta\psi'' \quad \text{when } \theta' = 0 ,$$

$$\gamma = a(b^2+d^2)^{1/2}(\cos\psi_a'' - \cos\psi_b'')/\Delta\psi'' + \tfrac{1}{2}b(b^2+d^2)^{1/2}(\sin^2\psi_b'' - \sin^2\psi_a'')/\Delta\psi'' ,$$

in which

$$a = \cos\theta'\cos\theta'' ,$$

$$b = \sin\theta'\sin\theta'' ,$$

$$c = \sin\theta'\cos\theta'' ,$$

$$d = \cos\theta'\sin\theta'' .$$

In these expressions (θ'', ψ'') are the polar angles of the $\vec{g}$ or $\vec{A}$ tensor symmetry axis z'' with respect to a reference frame tied to the crystal. The angle ψ'' is measured from the plane with respect to which the libration of the Cl_2^- is taking place. This is a {100} plane for the $H_D^{\{100\}}$ defect to be discussed in Sec. III B (see Fig. 1) and a {110} plane for the $H_D^{\{110\}}$ defect (see Sec. III C and also Fig. 1 of Ref. 26). The angle θ'' remains constant during the LM and $\Delta\psi'' = \psi_b'' - \psi_a'' < 90°$ is the librational amplitude. θ' is the angle between $\vec{H}$ and ⟨100⟩. Note that the "motional" expression (5) does not only depend on the magnitude but also on the sign of $A_\perp$ which is not the case for the static expression (3). The latter depends on $A_\perp^2$ and thus only on the magnitude of $A_\perp$. It follows that a motional analysis allows one in principle to determine the relative sign of the hf components, something a static analysis can not. Moreover, because we are dealing in this paper with Cl_2^- species for which the sign of $A_\parallel$ is known[19] (it is positive), we are able to determine the absolute sign of $A_\perp$.

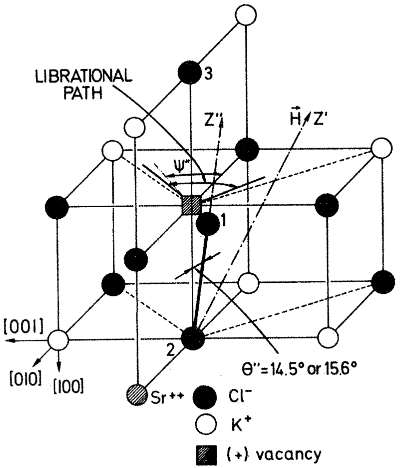

FIG. 1. Schematic three dimensional of the $H_D^{\{100\}}$ (Sr^{2+}) center in KCl:Sr^{2+}. The figure defines the various axes and angles used to describe the librational motion of the Cl_2^- with respect to a {100} plane. The Cl_2^-, composed out of chlorines Nos. 1 and 2, librates along almost a quadrant of a cone with constant apex angle θ''. For clarity, Cl No. 2 has been drawn on a lattice site.

B. The $H_D^{\{100\}}$ center

1. Analysis of the ESR *spectra*

A strong well defined ESR spectrum of the $H_D^{\{100\}}$ center is obtained in KCl:Sr^{2+} samples by an x irradiation at 77 K lasting several hours. Such a spectrum was not observed in KCl:Ba^{2+} and in KCl:Cd^{2+} samples subjected to a similar treatment. In KCl:Ca^{2+} and in KCl:Mg^{2+} the $H_D^{\{100\}}$ ESR spectrum is somewhat obscured by overlap with lines originating from, e.g., $H_D^{\{110\}}$ centers (see Sec. III C). In KCl:Pb^{2+} and KCl:Sn^{2+} the $H_D^{\{100\}}$ ESR spectra are strongly dominated by ESR lines belonging to V_K or Sn^+ centers.[14,27]

In Fig. 2 the $H_D^{\{100\}}$ (Sr^{2+}) ESR spectra recorded at 52 K are presented. The interfering V_K-center lines were routinely eliminated through an optical excitation of the F centers. The characteristic seven-groups-of-lines structure with a hyperfine (hf) separation of the order of 10.0 mT proves that one is dealing with Cl_2^- molecule ions. From an angular variation study it is concluded that the Cl_2^- internuclear axis makes a 14.5°± 1.0° angle with ⟨100⟩ in a {100} plane. The internuclear axis of a Cl_2^- species coincides with the direction of maximum hf separation. The second highest line and second lowest line are split, indicating that the two chlorine nuclei are inequivalent and that the Cl_2^- molecular bond is bent. This inequivalency as represented by $A_{\parallel,1} - A_{\parallel,2}$ is about 2.3 mT. A rough calculation of the bending angle gives $|\theta_1'' - \theta_2''| \simeq 3.4°$.

In the following, however, we present a simplified analysis in which it was assumed that the principal axes of $\vec{g}$ and $\vec{A}_i$ coincide with each other and with the internuclear Cl_2^- axis. Thus the inequivalency of the two nuclei is ignored by taking $|\vec{A}_1| = |\vec{A}_2|$ and, furthermore, bending is overlooked. It has been shown that a good quantitative analysis is possible with these assumptions.[26]

First a static analysis was performed of the $H_D^{\{100\}}$ (Sr^{2+}) ESR spectra. In order to decide whether or not this type of analysis gives a good fit, the "$A_\perp$ criterion" was used which is the following.[26] Having determined the g components and the $A_\parallel = \frac{1}{2}(A_{\parallel,1} + A_{\parallel,2})$ value (which is known to have a positive sign),[19] one can calculate from expressions (3) the $A_\perp$ values using the experimental

In this paper the following impurities are studied: $M^{2+}=\mathrm{Ca}^{2+}$, Ba^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, Sn^{2+}, and Mg^{2+}. Possible effects of varying dopant concentrations were not systematically investigated.

Defects were produced by x irradiation at 77 K using a Siemens tube with a tungsten target operating at 50 kV and 50 mA. The duration of the irradiation was typically one to two hours. Such long irradiation produces, besides the H_D-type defects, the well known F and V_K centers. The latter are routinely eliminated by optical excitation of the F centers: the freed F-center electrons are attracted by the positive-charged V_K centers and annihilate them. Before irradiation the samples were heated to about 400 °C for several minutes and then rapidly cooled down.

Other experimental details and a description of the ESR techniques can be found in Ref. 16. It may be emphasized that KCl was chosen because it possesses, together with KF, the narrowest ESR lines of all the alkali halides and thus yields the best resolved ESR spectra. Furthermore, the observed Cl_2^- and Cl_3^{2-} species have small hyperfine splittings (typically about 10 mT) which means that second-order shifts of the line positions are small.

III. ANALYSIS OF THE ESR SPECTRA OF THE H_D-TYPE CENTERS

A. General remarks on the ESR analysis

The ESR spectra described in the following originate in all cases except one from a Cl_2^- molecule ion. The ESR analysis of such species in which sometimes the two chlorine nuclei are inequivalent and/or the molecular bond is bent, has been described thoroughly several times before.[23,24] Consequently, many details of the often tedious analysis will be omitted or only touched upon lightly.

It has become clear recently that some low-symmetry Cl_2^- defects exhibit reorientation motions which, when fast enough, result in line broadening and motionally averaged ESR spectra.[25,26] Sometimes the presence of the latter is not obvious from the qualitative features of the ESR spectra, especially if the motion is a limited one such as a librational motion (LM) with respect to a crystal symmetry plane.[26] Such librational motions are encountered in the present investigation. In order to perceive their presence it is necessary to perform both a "static" and a "librational" analysis of the ESR spectra and see which one gives the best fit.

We briefly outline the procedure.[26] The Cl_2^- ESR spectra are described by the following spin-Hamiltonian (in the usual notation):

$$\frac{\mathcal{H}}{g_0\mu_B}=\frac{1}{g_0}\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S}+\sum_{i=1}^{2}\vec{S}\cdot\overleftrightarrow{A}_i\cdot\vec{I}_i\,, \tag{1}$$

where the summation is over the two chlorine nuclei. A static analysis describes the ESR spectra if the orientation of the Cl_2^- is fixed in the lattice or if the Cl_2^- moves (jumps, rotates, librates) with a rate or frequency that is sufficiently slow so as not to result in motional averaging. In this so-called static case the angular variation of the g factor and the first-order hyperfine separation, K_i, are given by the well known expressions (in axial symmetry approximation):

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

$$K_i^2(\theta)g^2(\theta)=A_{\parallel,i}^2 g_\parallel^2\cos^2\theta+A_{\perp,i}^2 g_\perp^2\sin^2\theta\,, \tag{3}$$

where $g_\parallel$, $g_\perp$ and $A_{\parallel,i}$, $A_{\perp,i}$ are the principal components of the $\overleftrightarrow{g}$ and the hyperfine $\overleftrightarrow{A}_i$ tensors. θ is the angle between the spin-Hamiltonian symmetry axis z'' and the direction z' of the external static magnetic field $\vec{H}$. θ can be either θ_g, θ_1, or θ_2 if the molecule is bent. Although all five defects described in this paper possess a symmetry lower than tetragonal or trigonal, they have been analyzed in an axial approximation. The $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ tensors are undoubtedly of orthorhombic character, but deviations from axial symmetry turn out to be rather small and often could not be reliably determined.

If the Cl_2^- reorients so fast that a motionally averaged ESR spectrum is produced, then the g factor and first-order hyperfine separation are given by the following "motional" expressions[26]:

$$\begin{aligned}\langle g\rangle^2&=[(g_\parallel-g_\perp)\alpha_g+g_\perp]^2\\&\quad+(g_\parallel-g_\perp)^2(\beta_g^2+\gamma_g^2)\end{aligned} \tag{4}$$

$$\begin{aligned}\langle K_i\rangle^2&=[(A_{\parallel,i}-A_{\perp,i})\alpha_i+A_{\perp,i}]^2\\&\quad+(A_{\parallel,i}-A_{\perp,i})^2(\beta_i^2+\gamma_i^2)\,,\end{aligned} \tag{5}$$

with

$$\begin{aligned}\alpha&=\langle\cos^2\theta\rangle\,,\\ \beta&=\langle\sin\theta\cos\theta\cos\psi\rangle\,,\\ \gamma&=\langle\sin\theta\cos\theta\sin\psi\rangle\,,\end{aligned} \tag{6}$$

in which (θ,ψ) are the polar angles of the spin-Hamiltonian symmetry axis z'' with respect to a set of axes (x',y',z') tied to the magnetic field $\vec{H}\parallel z'$. The averages in (6) must be performed over the reorientation path (in case of a continuous motion) or over all the discrete orientations (in case of a jumping motion). For complete spherical averaging, $\alpha=\beta=\gamma=\frac{1}{3}$.

In the case of a continuous librational motion and assuming that the axes of $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ coincide, expressions (6) may be written

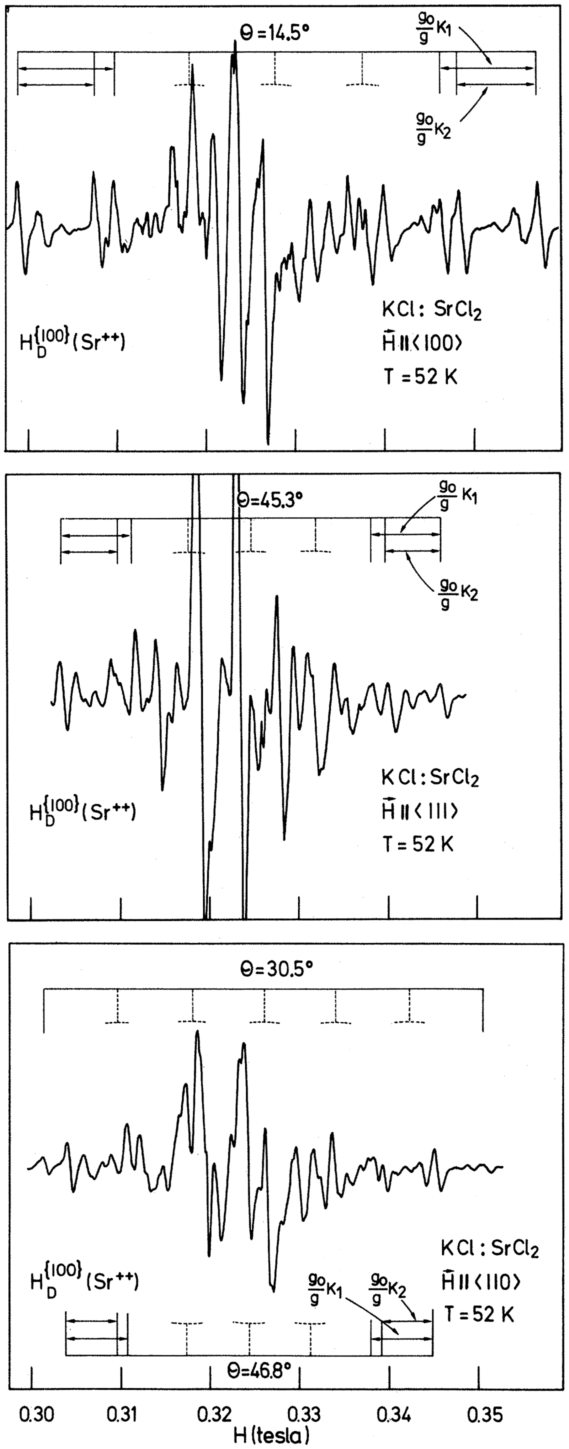

FIG. 2. ESR spectra of the $H_D^{\{100\}}$ (Sr^{2+}) center in $KCl{:}Sr^{2+}$ recorded at 52 K for three special orientations of the magnetic field $\vec{H}$. The microwave frequency $\nu = 9.16$ GHz. The Cl_2^- V_K centers were bleached out optically. Note that the angle θ corresponds to the measured values and not to the values resulting from a "librational" analysis of the ESR spectra.

first-order hf $K(14.5°)$, $K(45.3°)$, and $K(30.5°)$ values obtained from the $\vec{H}\|\langle 100\rangle$, $\vec{H}\|\langle 111\rangle$, and $\vec{H}\|\langle 110\rangle$ ESR spectra. Not only should the three $A_\perp$ values thus calculated be approximately equal to each other but they should also fall in the range of +0.7 to +1.6 mT. Indeed, the hf parameters of Cl_2^- species are very well known and they all invariably fall in this range.[5] The static analysis gives a bad fit as is illustrated by the following three values obtained for $A_\perp^2$ [in units of $(\mathrm{mT})^2$]: +9.7, +2.4, and −1.6. The negative sign especially is bad and cannot be eliminated. It is concluded that the Cl_2^- of $H_D^{\{100\}}(Sr^{2+})$ must exhibit a limited reorientation motion.

By assuming the simplest motion, namely a librational motion (LM) of the Cl_2^- with respect to the $\{100\}$ plane, it is possible to obtain a good fit of the ESR data using the $A_\perp$ criterion as a test. Indeed, a librational analysis employing expressions (4) and (5) and a librational amplitude $\Delta\psi'' = \psi_b'' - \psi_a''$ of about 75° yields the following $A_\perp$ values (in units of mT): +1.3, +1.5, and +1.6 deduced from $K(14.5°)$, $K(45.3°)$, and $K(30.5°)$, respectively, leading to a very good mean value $A_\perp = (+1.5 \pm 0.2)$ mT. The improvement in fit is so striking that we feel that the librational motion exists although the calculated size of the librational amplitude should be viewed with some caution. By using expressions (4) and (5) we have explicitly accepted that all positions on the librational path are equally probable. However, an equally good fit would have been obtained if we had assumed that the librational motion is a jumping motion between two discrete symmetric positions with respect to the $\{100\}$ plane. Only uniaxial stress measurements will be able to decide between the two possibilities.[26] Table I gives the results of the librational analysis of the $H_D^{\{100\}}(Sr^{2+})$. For the other $H_D^{\{100\}}$ centers the ESR data, as far as they could be determined, are also presented in Table I.

The $H_D^{\{100\}}$ ESR line shapes show a hint of unresolved superhyperfine (shf) structure. This is best observed in the ESR spectrum of $H_D^{\{100\}}(Ca^{2+})$ or $H_D^{\{100\}}(Sr^{2+})$ when $\vec{H}\|\langle 100\rangle$ and is very similar to the unresolved shf structure of the ESR lines of $H_D^{\{110\}}(Ca^{2+})$ in a $\langle 100\rangle$ direction (see Sec. III C). Figure 3(a) shows the latter line shape when $\vec{H}\parallel\langle 100\rangle$ ($\theta = 18.5°$): it is characteristic of an unresolved shf structure originating from several equidistant lines of equal intensity. Because for all interstitial and hole centers observed so far in the alkali halides, no shf structure resulting from the nuclei of alkali ions has ever been observed, it seems reasonable to conclude that the shf structure is a four-line structure originating from the interaction with a single chlorine nucleus. Resolved shf structures are observed for some $H_D^{\{110\}}$ centers

TABLE I. Spin-Hamiltonian parameters resulting from a "librational" analysis of the $H_D^{\{100\}}$ centers in KCl: (i) ignoring inequivalency of the nuclei and the bending of the molecular bond, and (ii) including inequivalency and bending. The hyperfine parameters (for ^{35}Cl) and the linewidth ΔH (between extrema of the first derivative) are given in mT. The observation temperature, T_{obs}, and the decay temperature, T_{dec}, are given in K.

Center	T_{obs}		$g_\parallel$	$g_\perp$	$A_{\parallel,1}$	$A_{\parallel,2}$	$A_{\perp,1}$	$A_{\perp,2}$	$\theta''_{\text{lib},1}$	$\theta''_{\text{lib},2}$	ΔH	T_{dec}
$H_D^{\{100\}}(\text{Ca}^{2+})$	49	(i)	2.002 ±0.001	2.038 ±0.002	+10.0 ±0.1		+1.1 ±0.5		16.6° ±0.5°		0.70 ±0.05	225
$H_D^{\{100\}}(\text{Sr}^{2+})$	62	(i)	2.0018 ±0.0005	2.038 ±0.002	+9.96 ±0.05		+1.5 ±0.2		15.6° ±0.5°		0.85 0.05	230
		(ii)			+11.1 ±0.1	+8.8 ±0.1	+1.6 ±0.5	+1.4 ±0.5	17.4° ±1.0°	14.0° ±1.0°		
$H_D^{\{100\}}(\text{Pb}^{2+})^{\text{a}}$	73	(i)	2.002 ±0.001	2.037 ±0.002	+10.2 ±0.1		1.5 ±0.5		20.7° ±0.5°		1.05 ±0.05	225
$H_D^{\{100\}}(\text{Mg}^{2+})^{\text{b}}$	77	(i)	≃2.002	-	≃+10.0		-		≃19°		0.9 ±0.1	230
$H_D^{\{100\}}(\text{Sn}^{2+})^{\text{a,b}}$	120	(i)	≃2.002	-	≃+10.5		-		≃22°		0.9 ±0.1	-

[a] No shf structure originating from $^{207}\text{Pb}^{2+}$ or $^{119}\text{Sn}^{2+}$ nuclei is observed in enriched KCl: $^{207}\text{Pb}^{2+}$ or KCl: $^{119}\text{Sn}^{2+}$ crystals.

[b] The results of a "static" analysis are given (see text).

to be discussed in the next section [see Fig. 3(b)].

The ESR properties of the $H_D^{\{100\}}$ center in KCl: Pb^{2+} and KCl:Sn^{2+} are surprising in one respect. Indeed, both ions are good traps for positive holes[12,15] resulting in Pb^{3+} ($6s^1, {}^2S_{1/2}$) and Sn^{3+} ($5s^1, {}^2S_{1/2}$) paramagnetic species which are characterized by very large hyperfine splittings. As a result one might expect that the ESR spectra of the H_D-type centers would show a superhyperfine structure due to the interaction of the unpaired hole of the interstitial Cl_2^- species with the nuclei of these divalent ions. Not a trace of such a structure was observed in KCl: $^{207}\text{Pb}^{2+}$ crystals (92% enriched $^{207}\text{Pb}^{2+}$ which has nuclear spin $\frac{1}{2}$) and KCl: $^{119}\text{Sn}^{2+}$ crystals (90% enriched $^{119}\text{Sn}^{2+}$ which has nuclear spin $\frac{1}{2}$). Electron-nuclear double-resonance experiments may throw some light on this matter.

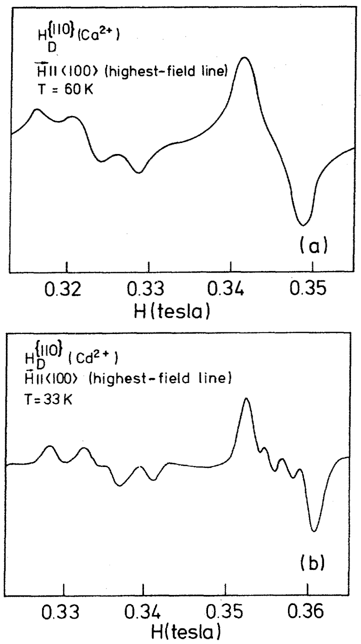

FIG. 3. (a) Two high-field lines of the $H_D^{\{110\}}$ (Ca^{2+}) center (^{35}Cl ^{35}Cl and ^{35}Cl ^{37}Cl species) for $\theta = 18.5°$ when $\vec{H} \parallel \langle 100\rangle$, exhibiting a hint of an unresolved four-line shf structure; (b) two high-field lines of the $H_D^{\{110\}}$ (Cd^{2+}) center for $\theta = 10.5°$ when $\vec{H} \parallel \langle 100\rangle$, exhibiting a resolved four-line shf structure.

2. *Model for the $H_D^{\{100\}}$ center*

As its name implies, the $H_D^{\{100\}}$ center is formed by the trapping of a mobile interstitial halogen atom (an H center)[1-3] by an $[M^{2+}, (+)]$ impurity complex consisting of a divalent cation, M^{2+}, and its associated charge-compensating positive-ion vacancy (+). The interstitial character is indicated by two observations: First, it takes a few hours of x irradiation to produce a high concentration of $H_D^{\{100\}}$ centers and second, optical excitation of F centers (produced at the same time during the x irradiation) which releases mobile electrons in the lattice, does not affect the $H_D^{\{100\}}$-center concentration. This indicates that it is either a neutral or a negatively charged defect. Both properties are shared by all interstitial halogen-atom centers observed so far such as H centers, H_A centers, and H_{AA} centers.[5]

The fact that the tipping angle of the $H_D^{\{100\}}$ centers varies with the M^{2+} dopant proves that the divalent cation is intimately involved in the defect structure. The specific model that we propose for $H_D^{\{100\}}$ is depicted in Fig. 4 for KCl : Sr^{2+}. The interstitial halogen atom is stabilized as a Cl_2^- molecule ion by an Sr^{2+} ion and a positive-ion vacancy which are nearest neighbors (NN) of one another. This model, which possesses C_{1h} symmetry, agrees with the experimental observations. In particular it permits a librational motion of the Cl_2^- with respect to the $\{100\}$ plane of the figure. Furthermore, the unresolved four-line shf structure is also readily explained. It originates from the interaction with the nucleus of the substitutional chloride ion No. 3 in Fig. 4. It is important to emphasize at this point that this four-line shf structure would be difficult to explain in a model *not* involving a positive-ion vacancy. A model without a positive-ion vacancy would in addition exert a strong Coulomb attraction on mobile electrons, which is not observed. Though the proposed structure is not the only possible one that is in agreement with the data, it is certainly the most simple and most compact one that can be constructed in a $\{100\}$ plane. There is, e.g., no need to propose a defect structure involving a dimer of $[M^{2+}, (+)]$ complexes.

If the model of Fig. 4 is correct it is somewhat surprising that this $H_D^{\{100\}}$ defect is not observed in KCl : Ba^{2+} and in KCl : Cd^{2+}. *A priori* there is no reason to believe that in these crystals the $[M^{2+}, (+)]$ complexes would not occur in the nearest-neighbor[28] configuration or that they would not trap and stabilize interstitial halogen atoms. This point was not studied further. It is conceivable that in KCl : Ba^{2+} and KCl : Cd^{2+}, interstitials are stabilized in a configuration other than $H_D^{\{100\}}$ symmetry. There are precedents for such a difference. In the $H_A(Na^+)$ center[29] in KCl : Na^+, the Cl_2^- lies in a $\{100\}$ plane while for the corresponding $H_A(Li^+)$ center[25] in KCl : Li^+ the Cl_2^- lies in a $\{100\}$ plane. It is also possible that in some crystals $H_D^{\{100\}}$ centers are not stable at 77 K and that they must be produced by x irradiation at lower temperatures.

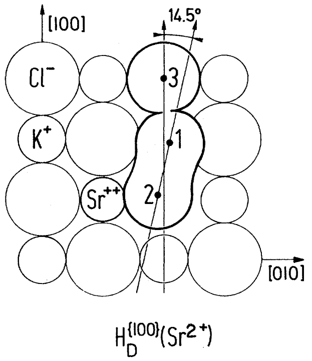

FIG. 4. Schematic two-dimensional model in a $\{100\}$ plane of the $H_D^{\{100\}}$ (Sr^{2+}) center in KCl:Sr^{2+}. Halogen nucleus No. 3 is responsible for the unresolved four-line shf structure. Bending of the Cl_2^- is not shown.

C. The $H_D^{\{110\}}$ center

1. Analysis of the ESR *spectra*

The $H_D^{\{110\}}$ center ESR spectrum is observed in KCl crystals doped with either Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, or Mg^{2+} ions. In KCl : Ba^{2+}, KCl : Cd^{2+}, and KCl : Mg^{2+} it is directly and dominantly produced by an x irradiation at 77 K. In KCl : Ca^{2+}, KCl : Sr^{2+}, and KCl : Pb^{2+}, however, one has to heat the specimens to about 230 K for several minutes after the 77-K x irradiation in order to form $H_D^{\{110\}}$. At 230 K, $H_D^{\{100\}}(Ca^{2+})$, $H_D^{\{100\}}(Sr^{2+})$, and $H_D^{\{100\}}(Pb^{2+})$ are observed to decay. This process is illustrated in Fig. 5, which represents an isothermal anneal at 222 K (and measured in ESR at 77 K) of a KCl : Sr^{2+} specimen x irradiated at 77 K.

Figure 6 shows the ESR spectra, recorded at 77 K, of the $H_D^{\{110\}}(Ba^{2+})$ center. Again the characteristic seven-line hf structure originating from a Cl_2^- species is observed. The splitting of the second highest line and of the second lowest line proves that the two chlorine nuclei are inequivalent and that the Cl_2^- bond is bent. The inequivalency of the nuclei as illustrated by $A_{\parallel,1} - A_{\parallel,2}$ gives the following values: 2.1 mT for $H_D^{\{110\}}(Ca^{2+})$,

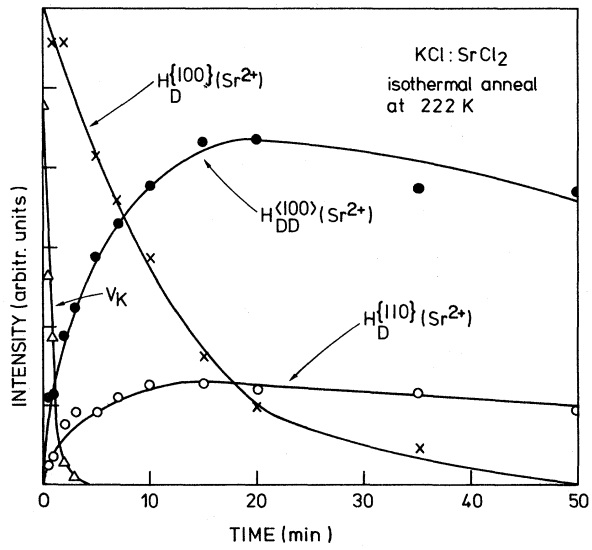

FIG. 5. Isothermal anneal at 222 K of a KCl:Sr^{2+} crystal x irradiated at 77 K for two hours. The data points were taken at 77 K.

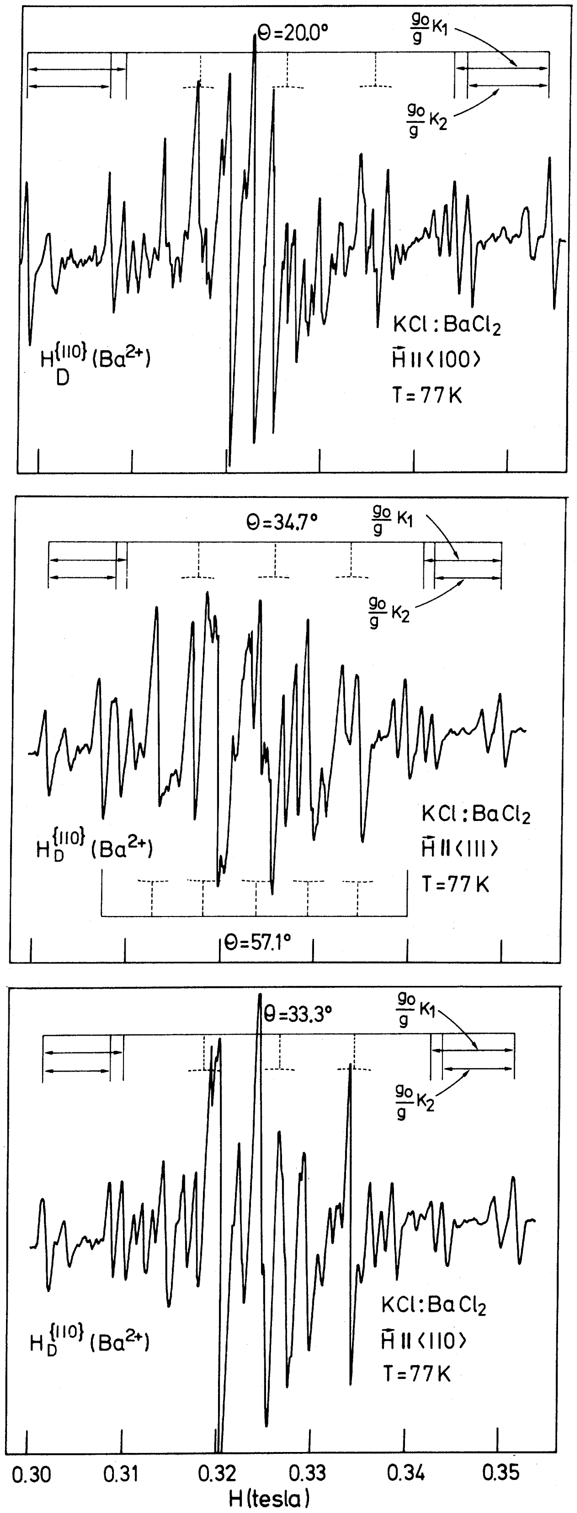

FIG. 6. ESR spectra at 77 K of the $H_D^{\{110\}}$ (Ba^{2+}) center in KCl:Ba^{2+} for three special orientations of the magnetic field $\vec{H}$.

1.4 mT for $H_D^{\{110\}}(\mathrm{Sr}^{2+})$, and 1.6 mT for $H_D^{\{110\}}(\mathrm{Ba}^{2+})$. The bending of the Cl_2^- bond is calculated to be small, and $|\theta_1'' - \theta_2''|$ is equal to ~1.1°, ~4.6°, and ~1.0° for Ca^{2+}, Sr^{2+}, and Ba^{2+} $H_D^{\{110\}}$ defects, respectively. For the $H_D^{\{110\}}$ centers in KCl doped with Cd^{2+}, Pb^{2+}, or Mg^{2+}, no good estimates of the inequivalency or the bending could be made. From here on we will ignore inequivalency and bending.

An angular-variation study of the ESR spectra shows that the Cl_2^- internuclear axis makes an angle θ_{stat}'' with ⟨100⟩ in a {110} plane. The following values (±1.0°) for θ_{stat}'' were found: 18.5°, 27.0°, 20.0°, 10.5°, 19.5°, and 6.0° for $H_D^{\{110\}}$ centers in KCl doped with Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, and Mg^{2+}, respectively.

A static analysis of the ESR spectra does not result in a good fit as evidenced by the "$A_\perp$ criterion." Indeed the calculated $A_\perp^2$ values are either too large or even negative. Consequently, a librational analysis was attempted in which it was assumed that the Cl_2^- performs a librational motion with respect to the {110} plane with an amplitude $\Delta\psi'' = \psi_b'' - \psi_a''$. Such a librational analysis gives a very good fit to the ESR data as shown by the following calculated $A_\perp$ values (±0.3 mT) for the Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Mg^{2+} $H_D^{\{110\}}$ centers: +1.1 mT, +1.0 mT, +1.3 mT, +1.5 mT, and +1.0 mT. As expected, the new tipping angles (±0.5°) have a somewhat larger value in the librational analysis than the measured ones: θ_{lib}'' is 19.0°, 28.9°, 21.0°, 10.6°, and 6.6° for Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Mg^{2+} $H_D^{\{110\}}$ centers, respectively. The librational amplitude is found to be in the neighborhood of 75° for all $H_D^{\{110\}}$ centers. The results are summarized in Table II. A relationship between $A_\parallel$ and θ'' is revealed: $A_\parallel$ increases along with θ''. A decrease of the peak-to-peak linewidth ΔH (for the ⟨100⟩ direction) along with increasing θ'' values is also observed. All ESR parameters show a particular temperature dependence: θ'' and $A_\parallel$ exhibit a small decrease with increasing temperature.

The lines of the $H_D^{\{110\}}$ defects show unresolved shf structure, especially in the spectra observed when $\vec{H}$ is along or near ⟨100⟩. In $H_D^{\{110\}}(\mathrm{Cd}^{2+})$ and $H_D^{\{110\}}(\mathrm{Mg}^{2+})$ this shf structure is well resolved. Figure 3(b) gives the four-line shf structure for the highest-field line of the $\theta = 10.5°$ $H_D^{\{110\}}(\mathrm{Cd}^{2+})$ ESR spectrum detected when $\vec{H} \parallel \langle 100\rangle$. As in all H-type centers observed so far, this small shf structure must originate from interaction with a supplementary chlorine nucleus. A computer simulation of Fig. 3(b) using Gaussian line shapes yields $k/\Delta H \simeq 1.1$ for the ratio of the superhyperfine splitting, k, to the linewidth ΔH. One deduces $k \simeq 0.22$ mT and $\Delta H \simeq 0.2$ mT. The shf structure is anisotropic: the lines observed when $\vec{H} \parallel \langle 111\rangle$ and $\vec{H} \parallel \langle 110\rangle$ show hardly any structure. One estimates

TABLE II. Spin-Hamiltonian parameters resulting from a "librational" analysis of the $H_D^{\{110\}}$ centers in KCl: (i) ignoring inequivalency of the nuclei and bending of the molecular bond, and (ii) including inequivalency and bending. The hyperfine parameters (for ^{35}Cl) and the linewidth ΔH (between extrema of the first derivative) are given in mT. The observation temperature, T_{obs}, and the decay temperature, T_{dec}, are given in K.

Center	T_{obs}		$g_\parallel$	$g_\perp$	$A_{\parallel,1}$	$A_{\parallel,2}$	$A_{\perp,1}$	$A_{\perp,2}$	$\theta''_{lib,1}$	$\theta''_{lib,2}$	ΔH	T_{dec}
$H_D^{\{110\}}(Ca^{2+})$	62	(i)	2.0016 ±0.0005	2.039 ±0.002	+10.15 ±0.05		+1.1 ±0.3		19.0° ±0.5°		0.78 ±0.05	255
		(ii)			+11.2 ±0.2	+9.1 ±0.2	+1.3 ±0.5	+1.5 ±0.5	18.3° ±0.5°	19.4° ±0.5°		
$H_D^{\{110\}}(Sr^{2+})$	75	(i)	2.0018 ±0.0005	2.033 ±0.002	+10.76 ±0.05		+1.0 ±0.3		28.9° ±0.5°		0.52 ±0.05	270
		(ii)			+11.4 ±0.2	+10.0 ±0.2	+1.6 ±0.5	+1.2 ±0.5	31.0° ±0.5°	26.4° ±0.5°		
$H_D^{\{110\}}(Ba^{2+})$	70	(i)	2.0018 ±0.0005	2.041 ±0.002	+10.18 ±0.05		+1.3 ±0.3		21.0° ±0.5°		0.78 ±0.05	240
		(ii)			+11.0 ±0.2	+9.4 ±0.2	+1.5 ±0.5	+1.4 ±0.5	20.5° ±0.5°	21.5° ±0.5°		
$H_D^{\{110\}}(Cd^{2+})$	81	(i)	2.0018 ±0.0005	2.038 ±0.004	+9.8 ±0.1		+1.5 ±0.5		10.6° ±0.5°		0.91 ±0.05	230
$H_D^{\{110\}}(Pb^{2+})^{a,b}$	77	(i)	~2.002		~+10.4				~19.5°		0.9 ±0.1	
$H_D^{\{110\}}(Mg^{2+})$	25	(i)	2.0018 ±0.0005	2.040 ±0.004	+9.9 ±0.1		±1.0 ±0.5		6.6° ±0.5°		0.94 ±0.05	230

[a] No shf structure originating from $^{207}Pb^{2+}$ nuclei is observed in enriched KCl: $^{207}Pb^{2+}$ crystals.

[b] The results of a "static" analysis are given (see text).

that $a_\parallel \simeq 0.2$ mT and $a_\perp \simeq 0.1$ mT. As in the case of the $H_D^{\{100\}}$ center no resolved or unresolved shf structure was observed in the $H_D^{\{110\}}(Pb^{2+})$ center originating from the Pb^{2+} nucleus.

2. *Model for the $H_D^{\{110\}}$ center*

The long x-irradiation times necessary to produce it and its imperviousness to electrons released in the lattice when F centers are optically excited, point again to the interstitial halogen-atom character of the $H_D^{\{110\}}$ center. The model that we propose is presented in Fig. 7. An interstitial halogen atom is stabilized as a Cl_2^- molecule ion on a negative-ion site by a divalent cation, M^{2+}, and a charge-compensating positive-ion vacancy (+). The difference with the $H_D^{\{100\}}$ model of Fig. 4 is that for the $H_D^{\{110\}}$ center the divalent cation and the positive-ion vacancy are next-nearest neighbors (NNN) of one another. The proposed structure is consistent with the following experimental data: (i) it is electrically neutral, (ii) it permits a librational motion with respect to the {110} plane, (iii) the tipping angle depends upon the dopant, and (iv) the chlorine nucleus responsible for the observed four-line shf structure is in a natural way supplied by chloride ion No. 3. The conversion from the $H_D^{\{100\}}$ to the $H_D^{\{110\}}$ center at 230 K implied by the data of Fig. 5 may be caused by a simple thermally activated jump of the positive-ion vacancy from an NN position to an NNN position with respect to the divalent cation and

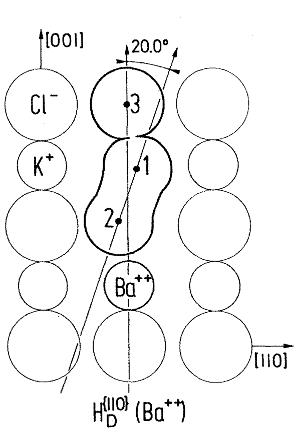

FIG. 7. Schematic two-dimensional model in a {110} plane of the $H_D^{\{110\}}$ (Ba^{2+}) center in KCl:Ba^{2+}.

accompanied by an appropriate reorientation of the Cl_2^- molecule ion.

The model may also explain the increasing shf interaction with decreasing θ'' as illustrated by ΔH in Table II. As θ'' decreases, the σ-type lobe of the Cl_2^- ground-state wave function points more and more towards chlorine No. 3, preferentially increasing the shf interaction with its nucleus.

Closer inspection of Fig. 7 shows that the $H_D^{\{110\}}$ center could in principle also possess a pyramidal motion (PM).[24,25]. In the case of $H_D^{\{110\}}(Ca^{2+})$ there is evidence for the existence of such PM. As the temperature is raised from 77 K to 177 K there is a rapid broadening and shifting of the ESR lines and there is an apparant decrease of the tipping angle θ'' by about 2°.

D. The di-interstitial $HI_D^{\langle 100\rangle}$ center

1. *Analysis of* ESR *spectra*

The $HI_D^{\langle 100\rangle}$ center is produced in $KCl:Sr^{2+}$ and $KCl:Ba^{2+}$ by an x irradiation at 77 K lasting a few hours. At the same time the $H_D^{\{100\}}(Sr^{2+})$ and the $H_D^{\{110\}}(Ba^{2+})$ centers, respectively, are produced. However the temperature range in which the $HI_D^{\langle 100\rangle}$ center is best observable in ESR, i.e., above 100 K, is quite different from the temperature region where the $H_D^{\{100\}}$ and $H_D^{\{110\}}$ are strongly observed, namely between 20 and 100 K. In the other doped crystals no $HI_D^{\langle 100\rangle}$ ESR signals were found after a similar treatment.

Figure 8 shows the ESR spectra of the $HI_D^{\langle 100\rangle}(Ba^{2+})$ center in $KCl:Ba^{2+}$ recorded at 140 K for $\vec{H}\parallel\langle 100\rangle$. Only for this magnetic field direction is a well defined spectrum observed. This ESR pattern possesses a striking resemblance to the ESR spectrum of the H center in KCl.[1-3] The qualitative analysis is in fact the same for both. Ignoring the finely spaced shf lines the spectrum consists out of a seven-line hyperfine pattern characteristic of a Cl_2^- species with two equivalent Cl nuclei. The shf structure originates from a further weak interaction with two other Cl nuclei which are also equivalent to each other. Even the linewidths ΔH are very comparable for the two centers.

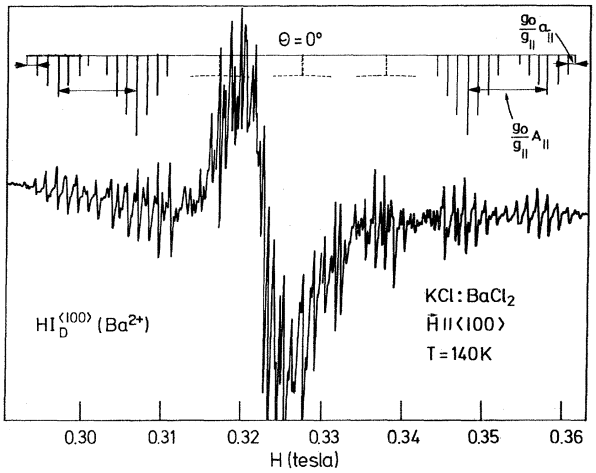

FIG. 8. ESR spectrum for $\vec{H}\parallel\langle 100\rangle$ of the $HI_D^{\langle 100\rangle}$ (Ba^{2+}) center in $KCl:Ba^{2+}$ recorded at 140 K.

There are, however, two important differences. First, the Cl_2^- in $HI_D^{\langle 100\rangle}$ is oriented exactly along $\langle 100\rangle$ whereas in the H center it lies exactly along $\langle 110\rangle$. Second, the well defined ESR pattern of Fig. 8 breaks down the more $\vec{H}$ moves away from the $\langle 100\rangle$ direction, indicating that the four Cl nuclei involved are no longer pairwise equivalent to each other with respect to the magnetic field direction. This means that the $HI_D^{\langle 100\rangle}$ center does not possess inversion symmetry.

No motional effects are apparent in the ESR spectra and so a static analysis was performed using spin-Hamiltonian (1) to which the following term was added:

$$\sum_{k=3}^{4}\vec{S}\cdot\overleftrightarrow{a}_k\cdot\vec{I}_k\,,$$

where the summation is over the two additional Cl nuclei responsible for the shf structure. Because of the complexity of the ESR spectra when $\theta\neq 0°$ the analysis was performed in the approximation that the two sets of Cl nuclei remained pairwise equivalent (i.e., bending of the various molecular bonds was ignored) and furthermore that $|\overleftrightarrow{A}_1| = |\overleftrightarrow{A}_2|$ and $|\overleftrightarrow{a}_3| = |\overleftrightarrow{a}_4|$. The latter conditions are clearly fulfilled when $\theta=0°$ and they very likely remain true for $\theta\neq 0°$ even if the bending of the bonds is taken into account. The results of the analysis are given in Table III.

2. *Model for the di-interstitial* $HI_D^{\langle 100\rangle}$ *center*

Attempts to construct a reasonable compact model for the $HI_D^{\langle 100\rangle}$ center which involves only a single trapped interstitial halogen atom do not lead anywhere. One is forced to consider di-interstitial models.[6,7] The specific structure that we propose for the $HI_D^{\langle 100\rangle}$ center is shown in Fig. 9. An interstitial chlorine atom and an interstitial chloride ion are trapped as a $\langle 100\rangle$ oriented Cl_2^- molecule ion by a divalent cation M^{2+} and a positive-ion vacancy (+), which are NN of one another. The model, which possesses C_{2v} symmetry around the M^{2+} to (+) axis, is consistent with the following experimental observations: (i) the long production time under x irradiation points to the interstitial or di-interstitial for that matter, character of the center, (ii) the center is negatively charged, mak-

TABLE III. Spin-Hamiltonian parameters of the various $HI_D^{\langle 100\rangle}$ centers in KCl. The hyperfine parameters (for ^{35}Cl) and the linewidth ΔH (between extrema of the first derivative) are given in mT. The observation temperature, T_{obs}, and the decay temperature, T_{dec}, are given in K. For comparison the Cl_2^- H-center data in KCl are included.

Center	T_{obs}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$a_{\parallel}$	$\lvert a_{\perp}\rvert$	ΔH	T_{dec}
$HI_D^{\langle 100\rangle}(\mathrm{Sr}^{2+})$[a]	120	2.0026 ±0.0003	2.027 ±0.003	+9.94 ±0.02	+1.4 ±0.5	+1.25 ±0.02	0.2 ±0.2	0.27 ±0.02	210
$HI_D^{\langle 100\rangle}(\mathrm{Ba}^{2+})$[a]	140	2.0024 ±0.0003	2.026 ±0.003	+10.02 ±0.02	+0.9 ±0.5	+1.24 ±0.02	0.3 ±0.2	0.26 ±0.02	260
H[b]	25	2.0018 ±0.0002	2.0224 ±0.0005	+10.86 ±0.01	+1.60 ±0.15	+0.74 ±0.01	0.27 ±0.01	0.12 ±0.01	42

[a] For the $HI_D^{\langle 100\rangle}$ center: $\vec{z} \parallel \langle 100\rangle$.

[b] For the H center: $\vec{z}'' \parallel \langle 110\rangle$ (from Ref. 2).

ing it repulsive for electrons freed by optical F-center excitation, as is indeed observed, (iii) the two chlorine nuclei, Nos. 1 and 2, are equivalent when $\vec{H} \parallel \langle 100\rangle$ but not when $\vec{H}$ deviates from that direction because the presence of both the M^{2+} and the vacancy destroys the inversion symmetry of the molecule and is likely to induce a sizable bending of the Cl_2^- molecular bond, and (iv) the shf interaction with the two equivalent (again for $\vec{H} \parallel \langle 100\rangle$) chlorine nuclei Nos. 3 and 4 is also explained in a natural way by the proposed model. One runs into difficulties in trying to explain this latter property if a dimer of $[M^{2+},(+)]$ complexes is proposed for the $HI_D^{\langle 100\rangle}$ center.

For these reasons we feel that the $HI_D^{\langle 100\rangle}$ model given in Fig. 9 is the most reasonable one. Note that the sense of the bending (towards or away from the M^{2+} ion) cannot be determined from the ESR data.

The $HI_D^{\langle 100\rangle}$ center may be looked upon as an $H_D^{\{100\}}$ center which has trapped an interstitial chloride ion, Cl_i^-. The latter is known as an I center, whence the notation $HI_D^{\langle 100\rangle}$. Finally, if this model is correct then $[\mathrm{Ba}^{2+},(+)]$ complexes which are NN of one another do occur in KCl : Ba^{2+}. The fact that no $H_D^{\{100\}}(\mathrm{Ba}^{2+})$ defect was found in Sec. III B seemed to point in the opposite direction. This point was not investigated further.

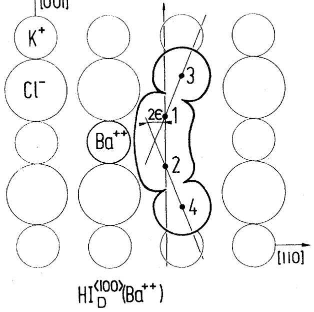

FIG. 9. Schematic two-dimensional model in a {100} plane of the di-interstitial $HI_D^{\langle 100\rangle}$ (Ba^{2+}) center in KCl:Ba^{2+}.

E. The $H_{DD}^{\{110\}}(\mathrm{Cl}_3^{2-})$ center

1. Analysis of ESR *spectra*

The $H_{DD}^{\{110\}}(\mathrm{Cl}_3^{2-})$ center has been observed so far only in KCl : Ba^{2+} samples. It is produced by x irradiating the crystal at 77 K for several hours followed by a warmup to about 230 K. Optical excitation of the F center does not affect the $H_{DD}^{\{110\}}$-center concentration.

The $H_{DD}^{\{110\}}(\mathrm{Cl}_3^{2-})$ ESR spectra are presented in Fig. 10. The main feature of these spectra is readily recognized for $\vec{H} \parallel \langle 100\rangle$: thirteen almost equidistant lines whose intensity ratios are close to $1:2:4:6:\cdots 6:4:2:1$. This hf pattern is explained if we assume that the paramagnetic entity is a linear symmetric Cl_3^{2-} molecule ion in which the hf interaction with the central chlorine nucleus is twice the hf interaction with the two other chlorine nuclei. Indeed, because chlorine nuclei possess nuclear spin $\frac{3}{2}$, such a choice of hf parameters generates a thirteen-line hf pattern with intensity ratios $1:2:4:6:7:8:8:8:7:6:4:2:1$. Closer inspection of the ESR spectra of Fig. 10 reveals that many of the chlorine isotope effects of the Cl_3^{2-} spectrum (^{35}Cl is 75% abundant and ^{37}Cl is 25% abundant) are resolved. The relative probabilities given between brackets for the various Cl_3^{2-} species are $^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{35}\mathrm{Cl}$ (27), $^{35}\mathrm{Cl}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ (18), $^{35}\mathrm{Cl}^{37}\mathrm{Cl}^{35}\mathrm{Cl}$ (9), $^{37}\mathrm{Cl}^{37}\mathrm{Cl}^{35}\mathrm{Cl}$ (6), $^{37}\mathrm{Cl}^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ (3), and $^{37}\mathrm{Cl}^{37}\mathrm{Cl}^{37}\mathrm{Cl}$ (1).

A careful angular-variation study shows that the Cl_3^{2-} molecular axis makes a 6.0° ± 1.0° angle with a $\langle 110\rangle$ direction in a {110} plane. Thus a 6.0°, a

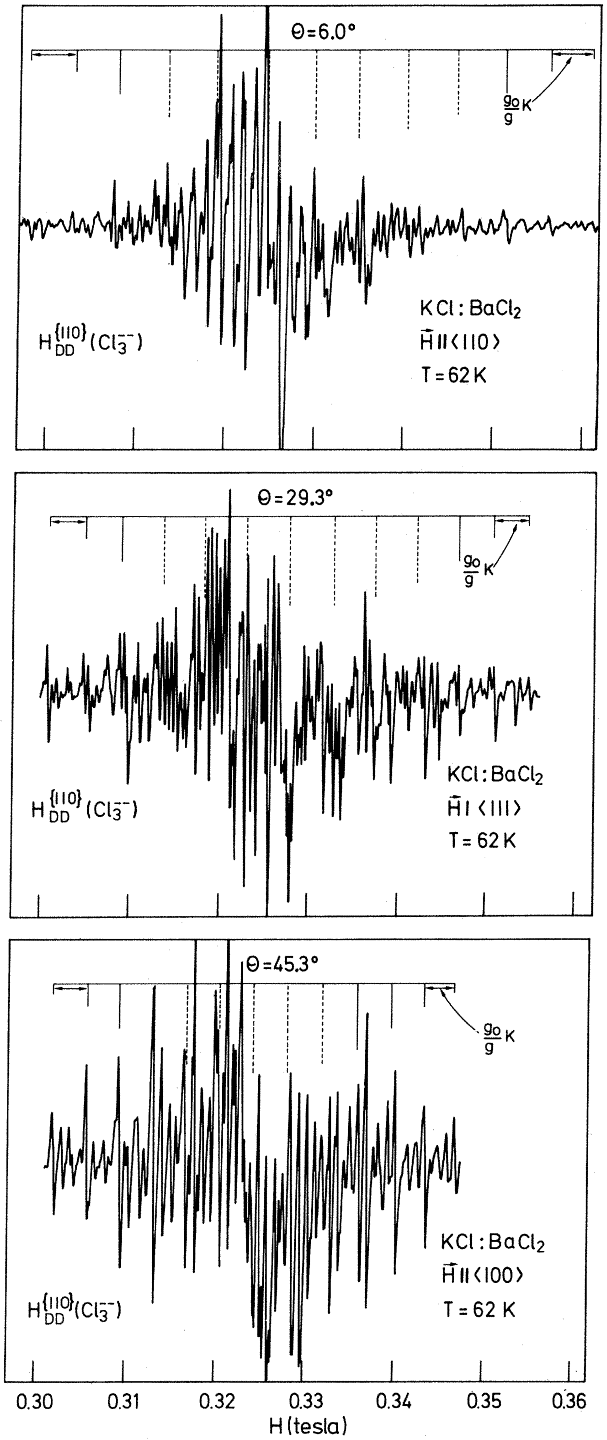

FIG. 10. ESR spectra at 62 K of the $H_D^{\{110\}}$ (Cl_3^{2-}) center in KCl:Ba^{2+} for three special orientations of the magnetic field $\vec{H}$.

29.3°, or a 45.3° spectrum is measured when the static magnetic field is along a ⟨110⟩, a ⟨111⟩ or a ⟨100⟩ direction, respectively. The angular variation also indicates that the two outer nuclei remain to a high degree, if not exactly, equivalent to each other for all directions of the magnetic field.

The ESR spectra were fitted to the following spin-Hamiltonian:

$$\frac{\mathcal{H}}{g_0\mu_B}=\frac{1}{g_0}\vec{H}\cdot\vec{\vec{g}}\cdot\vec{S}+\sum_{i=1}^{3}\vec{S}\cdot\vec{\vec{A}}_i\cdot\vec{I}_i\,,$$

where $\vec{\vec{A}}_1$ is the hf tensor of the central chlorine nucleus. The fitting to the experimental data was performed, assuming a perfectly linear Cl_3^{2-} molecule ion and $|\vec{A}_1|=2|\vec{A}_2|\equiv 2|\vec{A}_3|$. The results are given in Table IV. Thus, just about half the unpaired hole density resides on the central chlorine of the Cl_3^{2-}. This is very comparable to the situation for interstitial and di-interstitial $BrCl_2^{2-}$ centers in KCl:Br^- where the central bromine had about half of the unpaired hole density.[7] The ground state of a Cl_3^{2-} is $^2\Sigma_u$ and its electronic structure is analogous to that of $BrCl_2^{2-}$, which was discussed in Ref. 7.

2. *Model for the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center*

The exact equivalence of the two outer chlorine nuclei implies that the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center must possess inversion symmetry. It is impossible to construct a model using only a single $[M^{2+},(+)]$ complex. Therefore, the model that we propose involves a dimer of such complexes. It is shown in Fig. 11. An interstitial chlorine atom (No. 1) has been trapped by a dimer of $[M^{2+},(+)]$ complexes in a {110} plane in a configuration possessing inversion symmetry. Each positive-ion vacancy of the dimer is NN to a divalent cation and NNN to the other divalent cation. The interstitial chlorine atom No. 1 is stabilized as a Cl_3^{2-} by forming molecular bonds of equal strength with the two substitutional chloride ions Nos. 2 and 3. The model is electrically neutral which is consistent with its indifference towards optical *F*-center excitation. It also accounts in a natural way for the observed tilting. The presence of the vacancies and the Ba^{2+} ions exerts in this configuration a torque on the Cl_3^{2-} molecule, tilting it away from ⟨110⟩ in a {110} plane. The chlorine nuclei are related to each other by inversion and are consequently always equivalent to each other. The $H_{DD}^{\{110\}}(Cl_3^{2-})$ has D_{2h} symmetry with the twofold axis perpendicular to the plane of Fig. 11.

The fact that $H_{DD}^{\{110\}}(Cl_3^{2-})$ centers are found only after a warmup to about 230 K (following an x irradiation at 77 K) may indicate that positive-ion-vacancy jumps and/or divalent-cation- and positive-ion-vacancy interchanges are needed to bring two $[M^{2+},(+)]$ complexes into a suitable dimer configuration. It is also possible that the center is formed by retrapping of a mobile interstitial halogen atom.

TABLE IV. Spin-Hamiltonian parameters of the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center in KCl: Ba^{2+}. The hyperfine parameters (for ^{35}Cl) and the linewidth ΔH (between the extrema of the first derivative) are given in mT. The observation temperature, T_{obs}, and the decay temperature, T_{dec}, are given in K. For comparison, data on the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$ in KCl are included.

Center	T_{obs}	$g_\parallel$	$g_\perp$	$A_{\parallel,1}$[a]	$A_{\perp,1}$[a]	$A_{\parallel,2} \equiv A_{\parallel,3}$	$A_{\perp,2} \equiv A_{\perp,3}$	ΔH	T_{dec}
$H_{DD}^{\{110\}}(Cl_3^{2-})$[b]	55	2.0016 ±0.0005	2.045 ±0.002	+10.50 ±0.1	+1.7 ±1.0	+5.25 ±0.05	+0.9 ±0.5	0.30 ±0.05	265
$H_{AA}(Na^+)$ type $BrCl_2^{2-}$[c]	77	1.9893 ±0.0003	2.076 ±0.003	+50.21 ±0.02	+4.1 ±1.2	+5.62 ±0.05	+1.6 ±0.1	0.50 ±0.05	185

[a] Nucleus No. 1 is the central Cl nucleus in Cl_3^{2-} and the central Br nucleus in $BrCl_2^{2-}$.

[b] For the $H_{DD}^{\{110\}}(Cl_3^{2-})$, $\vec{z}'' \parallel (\langle 110\rangle + 6°$ in $\{110\})$.

[c] For the $H_{AA}(Na^+)$-type $BrCl_2^{2-}$, $\vec{z}'' \parallel \langle 110\rangle$ (from Ref. 7).

F. The $H_{DD}^{\langle 100\rangle}$ center

1. *Analysis of* ESR *spectra*

The $H_{DD}^{\langle 100\rangle}$ center has been observed only in KCl:Sr^{2+}, in KCl:Ba^{2+}, and in KCl:Cd^{2+} samples after x irradiation at 77 K and a subsequent warm-up to 240 K. It is observed in KCl:Sr^{2+} that the $H_{DD}^{\langle 100\rangle}$ center is more strongly formed in crystals with a high impurity concentration. There appears to be no direct relationship between the decay of one of the foregoing defects and the formation of $H_{DD}^{\langle 100\rangle}$. Optical excitation of the F centers does not affect the $H_{DD}^{\langle 100\rangle}$ concentration, pointing to either a neutral or a negatively charged character of the defect.

The ESR spectrum of the $H_{DD}^{\langle 100\rangle}(Ba^{2+})$ center in KCl:Ba^{2+} is presented for $\vec{H} \parallel \langle 100\rangle$ at $T = 60$ K in Fig. 12. The similarity with the Cl_2^- V_K center in KCl is striking.[27] For all orientations of the external magnetic field, the seven-line hf pattern with intensity ratios 1 : 2 : 3 : 4 : 3 : 2 : 1 characteristic of a Cl_2^- species with equivalent nuclei is observed. As in the case of the V_K center the lines are very narrow (0.2 mT) so that all chlorine isotope effects are resolved. However, there is one striking difference: Whereas the Cl_2^- of the V_K center is exactly $\langle 110\rangle$ oriented, the Cl_2^- in $H_{DD}^{\langle 100\rangle}$ is exactly along the $\langle 100\rangle$ direction.

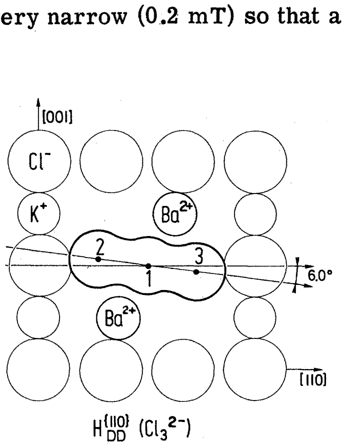

FIG. 11. Schematic two-dimensional model in a $\{110\}$ plane of the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center in KCl:Ba^{2+} involving a dimer of $[Ba^{2+}, (+)]$ complexes.

The ESR data were fitted to spin-Hamiltonian (1). A static analysis gives a good fit and the results are presented in Table V. The $A_\parallel$ values depend on the divalent impurity and they are smaller than the $A_\parallel = 10.13$ mT value of the V_K center.

2. *Model for the $H_{DD}^{\langle 100\rangle}$ center*

The fact that the chlorine nuclei of the $H_{DD}^{\langle 100\rangle}$ center are equivalent for all orientations of the magnetic field implies perfect inversion symmetry for the $H_{DD}^{\langle 100\rangle}$ center. For the same reason as given in the case of the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center we are led to construct a model involving a dimer of $[M^{2+}, (+)]$ complexes.

The model that we propose is presented in Fig.

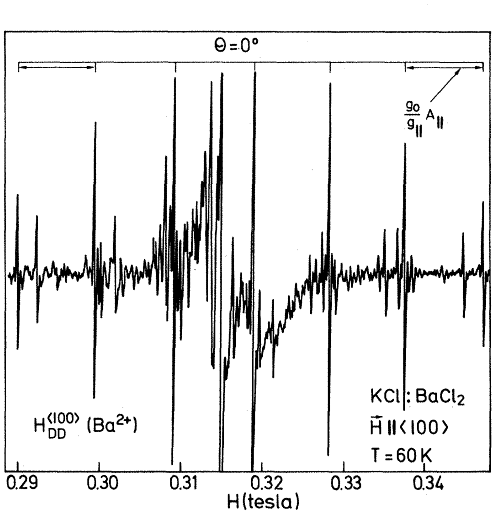

FIG. 12. ESR spectrum at 60 K of the $H_{DD}^{\langle 100\rangle}(Ba^{2+})$ center in KCl:Ba^{2+} for $\vec{H} \parallel \langle 100\rangle$.

TABLE V. Spin-Hamiltonian parameters of the various $H_{DD}^{\langle 100\rangle}$ centers in KCl. The hyperfine parameters (for ^{35}Cl) and the linewidth ΔH (between extrema of the first derivative) are given in mT. The observation temperature, T_{obs}, and the decay temperature, T_{dec}, are given in K. For comparison, data on the Cl_2^- V_K center in KCl are included.

Center	T_{obs}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	ΔH	T_{dec}
$H_{DD}^{\langle 100\rangle}(Sr^{2+})$ [a]	100	2.0023 ±0.0002	2.028 ±0.001	+9.70 ±0.02	1.1 ±0.3	0.23 ±0.05	255
$H_{DD}^{\langle 100\rangle}(Ba^{2+})$ [a]	60	2.0034 ±0.004	2.030 ±0.002	+9.34 ±0.05	+1.0 ±0.5	0.23 ±0.05	265
$H_{DD}^{\langle 100\rangle}(Cd^{2+})$ [a]	64	2.0025 ±0.0002	2.029 ±0.001	+9.86 ±0.02	+1.3 ±0.3	0.27 ±0.05	230
V_K [b]	77	2.00145 ±0.00005	2.0435 ±0.0001	+10.131 ±0.005	+1.213 ±0.05	0.14 ±0.03	210

[a] For the $H_{DD}^{\langle 100\rangle}$ centers: $\vec{z}'' \parallel \langle 100\rangle$.

[b] For the V_K center: $\vec{z}'' \parallel \langle 110\rangle$ (from Ref. 19).

13. It consists of a Cl_2^- molecule ion on a negative-ion site, perfectly ⟨100⟩ oriented and flanked in a {100} plane by two $[M^{2+},(+)]$ complexes. This dimer has for the $H_{DD}^{\langle 100\rangle}$ center a different configuration than in the case of the $H_{DD}^{\{110\}}(Cl_3^{2-})$ center. For the latter the dimer lies in a {110} plane whereas in the former it lies in a {100} plane. In this case both positive-ion vacancies of the dimer are NN to both divalent cations.

The experimental observations are readily explained by the model. It possesses inversion symmetry, D_{2h} in fact, and it is electrically neutral. Because the Cl_2^- is flanked by two positive-ion vacancies along its ⟨100⟩-oriented internuclear axis the chlorine ions Nos. 3 and 4 do not give rise to a resolved or an unresolved shf structure. This explains the narrow $H_{DD}^{\langle 100\rangle}$ ESR lines. The Cl_2^- is a perfectly linear molecule ion because there is an M^{2+} impurity at each side. Finally, because the Cl_2^- is not crowded along its ⟨100⟩ molecular axis, the internuclear distance should be larger than in the case of, e.g., the H center or the $H_D^{\{100\}}$ center, resulting in substantially smaller $A_{\parallel}$ values as is indeed observed.

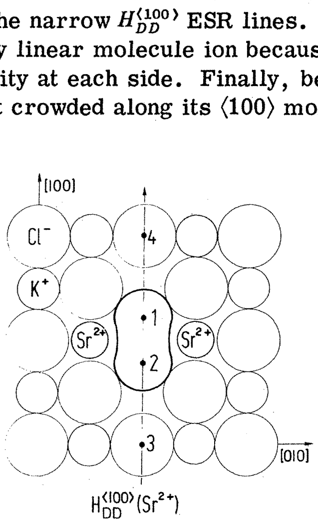

FIG. 13. Schematic two-dimensional model in a {100} plane of the $H_{DD}^{\langle 100\rangle}$ (Sr^{2+}) center in KCl:Sr^{2+} involving a dimer of $[Sr^{2+},(+)]$ complexes.

The model is compact and therefore appealing. The center is probably formed by the trapping of an interstitial chlorine atom (No. 1) by a substitutional chloride ion (No. 2) which is surrounded by a dimer of $[M^{2+},(+)]$ complexes. The warmup to 240 K which is necessary to produce it, may indicate that a rearrangement of the two $[M^{2+},(+)]$ complexes with respect to each other must take place before the configuration of Fig. 13 is reached.

IV. CONCLUDING REMARKS

The models for the H_D-type centers that are proposed in this paper are not the only ones that one can think of, but they are, we believe, the most probable ones. The presence in these models of at least a single $[M^{2+},(+)]$ complex is clearly established. Indeed, the ESR parameters, the tipping angle in particular, depend upon the divalent impurity. In fact it is worth emphasizing that we have not found any trace of a defect whose ESR parameters are independent of the divalent cation. An obvious example would be an interstitial halogen atom trapped by an isolated positive-ion vacancy. There seems to be no reason why such a center could not exist.[30] The fact that none have been observed is very likely because most positive-ion vacancies are used as charge compensators. As a result there is no competitive concentration of isolated anion vacancies. Another, though less likely factor may be that such a $[Cl_i^0,(+)]$ defect is not stable at 77 K which is the lowest temperature at which our *x* irradiations could be performed.

The positive-ion vacancy can be either in a nearest-neighbor or a next-nearest-neighbor position to the M^{2+} ion. In fact, both configurations are used in the models for the $H_D^{\{100\}}$ and for the $H_D^{\{110\}}$ centers, respectively. More information about the structure of these centers and about the presence and type of librational motion (i.e., a jumping motion or a continuous motion) can undoubtedly be obtained from a correlation of the ESR data with polarized optical absorption measurements and from uniaxial stress experiments at very low temperatures both in ESR and optical absorption. In any case it will be difficult to obtain precise information on the position of the anion vacancy with respect to the M^{2+} ion *before* trapping of the interstitial halogen atom. There may be a difference in trapping cross section for both $[M^{2+}, (+)]$ configuration may change in the process of trapping an interstitial halogen atom.

Dimer configurations of $[M^{2+}, (+)]$ complexes are involved in the proposed models for the $H_{DD}^{\{110\}}$ (Cl_3^{2-}) and $H_{DD}^{\langle 100\rangle}$ centers. The compelling reason for this derives from the observation that, as accurately as can be ascertained, these defects possess inversion symmetry. Though no search for H_D-type centers involving trimers of complexes was made, it is possible that such centers may be produced by suitable aging or heating-cooling cycles of the samples before *x* irradiation. In any case it appears that H_D-type centers may be used as probes in studies of agglomeration kinetics of $[M^{2+}, (+)]$ complexes and the formation of Suzuki phases.

For the $HI_D^{\langle 100\rangle}$ centers a di-interstitial halogen model involving a single $[M^{2+}, (+)]$ complex is proposed. The essential constituent is a Cl_2^- molecule ion which possesses weak additional bonds with two chloride ions along the ⟨100⟩-oriented molecular axis. The model is somewhat unusual in that the negatively charged Cl_2^- is positioned very near a site which is a positive-ion vacancy in the unperturbed lattice.

Because in ESR we are observing only paramagnetic species (Cl_2^- and Cl_3^{2-}), we are seeing only a part of the complex defects that are produced by the *x* irradiation. For instance, it is quite probable that for every defect containing a Cl_2^- or Cl_3^{2-} molecule ion, a similar defect containing a diamagnetic Cl_2 or Cl_3^- species exists. From optical absorption measurements in the 200–300 nm region, evidence exists for the presence of such molecules.[20,31] Another surprising observation which merits attention is that no H_D-type centers were detected in KCl : Zn^{2+} crystals. The reason for this is not known.

Finally, we should mention that if Br^- impurities are present in KCl : M^{2+} (usually between 50 to 100 ppm is present in nominally pure KCl) that $H_D^{\{100\}}$- and $H_D^{\{110\}}$-type $BrCl^-$ centers are formed. These defects were not further investigated. However, their study might contribute valuable new insight into the structure and properties of the Cl_2^- H_D-type centers.

ACKNOWLEDGMENTS

The authors wish to thank F. Van Steen and E. Goovaerts for very helpful discussions and A. Bouwen for his excellent experimental support. One of us (W.V.P.) wishes to thank the IWONL (Instituut voor Wetenschappelijk Onderzoek in Nijverheid en Landbouw) for a scholarship. We also wish to thank the IIKW (Interuniversitair Instituut voor Kernwetenschappen) and the NFWO (Nationaal Fonds voor Wetenschappelijk Onderzoek) for financial support.

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[30] The F_3^{2-} center (called V_t center) observed in x-irradiated LiF by Cohen, Känzig, and Woodruff [J. Phys. Chem. Solids 11, 120 (1959)], may in our opinion be a center formed by the trapping of an interstitial F_i^0 by an isolated positive-ion vacancy. The model proposed by Cohen, Känzig, and Woodruff involving trivacancy and based on the erroneous conclusion that F_3^{2-} possesses a $^2\Pi$ ground state seems quite unrealistic. The recent theoretical analysis by Jette and Adrian [Phys. Rev. Lett. 43, 1119 (1979)] correctly assigns a $^2\Sigma_u$ ground state to the F_3^{2-} molecule ion in agreement with the conclusions of Ref. 7 on $BrCl_2^{2-}$ and the Cl_3^{2-} analysis in the present paper. However, the implication by Jette and Adrian that this ⟨110⟩-oriented F_3^{2-} represents another manifestation of the pure interstitial fluorine-atom center (*H* center) different from the well established ⟨111⟩-oriented F_2^- *H* center (Ref. 3) is, we believe, not correct.

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