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Electron-spin resonance of a complex $Pb^+(6p^1)$ defect in alkali halides

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The electron-spin-resonance spectra are analyzed of a Pb^+ defect produced by a long x-ray irradiation below 150 K in Pb^{2+}-doped KCl and RbCl. At liquid-helium temperatures the main symmetry axis of the center is tipped a few degrees away from $\langle 001 \rangle$ in a $\{110\}$ plane. At higher temperatures the center exhibits a librational motion which averages out the tipping effects but leaves the spectra with a small orthorhombic component. A model is proposed which is in agreement with these facts and with the behavior of the hyperfine components: A substitutional Pb^+ possessing weak molecular bonds with two adjoining substitutional Cl^- ions is perturbed by an interstitial Cl^- ion in a next-nearest interstitial tetrahedral site. The analysis of the hyperfine data confirms a general property of the np^1 ($n=4,5,6$) heavy metal ions and atoms: The electron-spin density at the nucleus is large and negative.

I. INTRODUCTION

The $Sn^+(5p^1)$ ion was the first of the np^1 ($n=4,5,6$) heavy metal impurities whose electron-spin-resonance (ESR) spectrum was detected in the alkali halides.[1] This primary Sn^+ is strongly produced by a short (~ 10 min) x-ray irradiation at 77 K in, e.g., Sn^{2+}-doped KCl. Because the Sn^{2+} is associated with a charge-compensating cation vacancy, there are in fact three primary Sn^+ centers: First, a Sn^+(NN) with a cation vacancy in a nearest-neighbor (NN) position; second, a Sn^+(NNN) with such vacancy as a next-nearest neighbor (NNN); and finally an unperturbed Sn^+(tetrag) center. The Sn^+ defects manifest themselves as $\langle 100 \rangle$ oriented symmetric $SnCl_2^-$ molecule ions and the cation vacancy represents a small perturbation in the plane perpendicular to the molecular axis.[1]

Primary $Pb^+(6p^1)$ centers of identical structure should also exist and optical absorption investigations strongly support their presence.[2] However, a search for their ESR spectra has been particularly unsuccessful. This is also the case for the primary $Tl^0(6p^1)$ center and a possible explanation for this has been suggested recently.[3]

A continued ESR investigation of heavy metal impurities has yielded a bewildering variety of defects. This is particularly true if the doped alkali halides are x-ray irradiated above 220 K, the temperature at which negative-ion vacancies become mobile. Next to several very complicated[1] Sn^+ and[4] Pb^+ ESR spectra the resonance patterns of[5] complex $Sn^-(5p^3)$ and[6] $Pb^-(6p^3)$ centers were found in KCl, the first possessing a dynamic Jahn-Teller effect and the second a strong static one. The analysis of the complex np^1 centers proved to be more tractable initially for the atomic $Tl^0(6p^1)$, $In^0(5p^1)$, and $Ga^0(4p^1)$ defects, and these were investigated first.[3,7–10] They have been proven since to be attractive laser-active centers for near-infrared lasers[11,12] (1.3–1.9 μm). The detailed study of their properties is a matter of current interest.[13,14] At sufficiently high Tl^+ concentrations substitutional and interstitial Tl_2^+ centers are formed.[15,16]

The present paper discusses the ESR properties of a $Pb^+(6p^1)$ defect.[4] It is neither one of the many produced by x-ray irradiation above 220 K where anion vacancies are mobile nor is it one of the three possible primary Pb^+ centers. It is produced by a rather long x-ray irradiation at 77 K and it will be argued that an interstitial halogen ion is involved in the model. This center also possesses some subtle motional properties (Sec. III B) the analysis of which has contributed to establishing the structure of the center. Note that the ability of Pb^{2+}-cation vacancy complexes to stabilize interstitial halogens is well established.[2,17–20]

II. EXPERIMENTAL

The crystals used in these experiments were grown by the Kyropoulos and the Bridgman methods. Usually about 1 wt. % $PbCl_2$ was added to the KCl and RbCl melts. In order to minimize the possible influence of oxygen or hydroxyl impurities a few crystals were grown in vacuum in a closed-quartz ampule from material purified by processing it in a reactive atmosphere.[16,21] Some of the crystals doped with 92% enriched $^{207}Pb^{2+}$ were grown this way. The defects were produced by a tungsten x-ray source operating at 50 kV and 50 mA. The other experimental details are the same as in Ref. 7.

III. Pb^+ ESR SPECTRA

A. Quantitative analysis

The Pb^+ center to be discussed in this paper and which we shall name $Pb^+(Cl_i^-)$ in Sec. V is observed in $KCl:Pb^{2+}$ and $RbCl:Pb^{2+}$ after x-ray irradiation at 77 K. An important observation is that the concentration builds up rather slowly: After 3 h of irradiation the Pb^+ intensity is still increasing linearly with time. Figure 1 presents the Pb^+ ESR spectra taken at 9 K. The spectra are indicated by the angle θ between the external magnetic field $\vec{H}$ and the symmetry axis z of the center.

Natural occurring Pb possesses 79% of even-A Pb isotopes which have no nuclear spin. They give rise to the single anisotropic resonance lines indicated in Fig. 1. The 21% abundant ^{207}Pb isotope possesses nuclear spin $I=\frac{1}{2}$

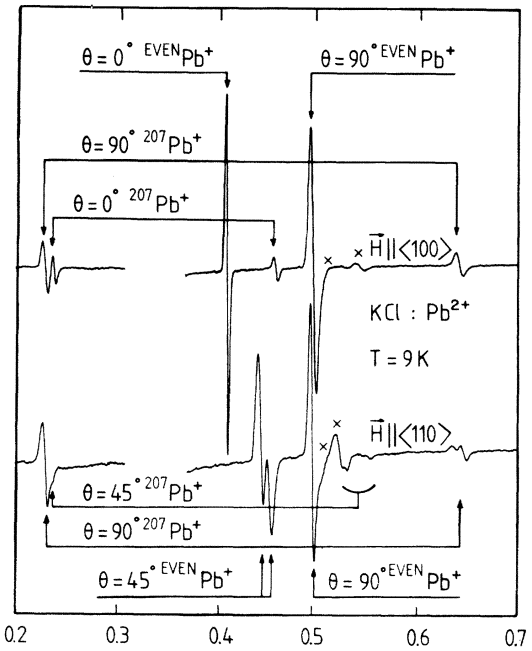

FIG. 1. ESR spectra of the $Pb^{+}(Cl_i^{-})$ center in $KCl{:}Pb^{2+}$ taken at 9 K and at 9.16 GHz for two orientations of the static magnetic field $\vec{H}$. Sample had been x-ray irradiated for several hours at 77 K.

and as a result a hyperfine (hf) doublet is observed as indicated again in Fig. 1. In similar ESR experiments on KCl and RbCl doped with ∼92% enriched ^{207}Pb the two hf lines are indeed about 5 times stronger than the single even-A Pb^{+} lines. This is shown in Fig. 2. There is no doubt that but a single Pb nucleus is involved in the defect.

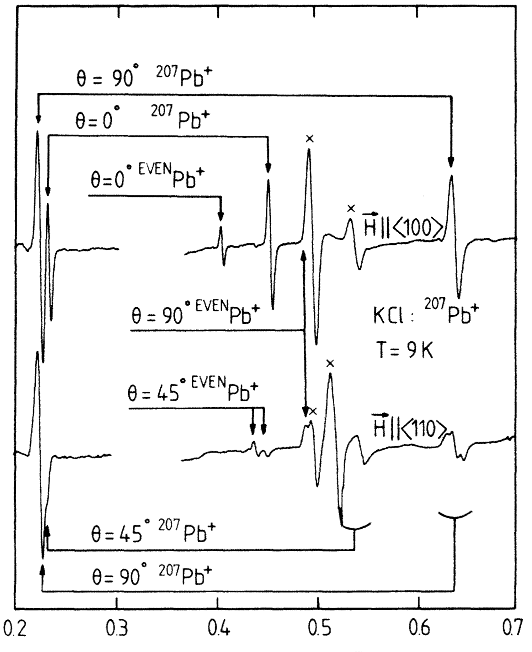

FIG. 2. $Pb^{+}(Cl_i^{-})$ ESR spectra in a 92% isotope enriched $KCl{:}^{207}Pb^{2+}$ crystal at 9 K, clearly showing the ^{207}Pb hyperfine doublets. Lines marked by a cross × (they are also noticeable in Figs. 1, 3, and 4) belong to an axial spectrum of an unidentified center.

From the angular variation of the spectra one deduces that the Pb^{+} center possesses at 9 K nearly axial symmetry but that the symmetry axis z is tipped away from $\langle 100\rangle$ in a $\{110\}$ plane by an angle of 2.5°±0.1° in KCl and 7.0°±0.2° in RbCl. This tipping feature is responsible for the splitting into two components of the $\theta=45°$ lines observed in Figs. 1 and 2 for $\vec{H}\,||\,\langle 110\rangle$.

The ESR spectra were fitted to a $S=\frac{1}{2}$, $I=\frac{1}{2}$ spin-Hamiltonian of the form (usual notation)

$$\frac{\mathcal{H}}{g_0\mu_B}=\frac{1}{g_0}\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S}+\vec{S}\cdot\overleftrightarrow{A}(^{207}\mathrm{Pb})\cdot\vec{I}\ , \tag{1}$$

using a numerical computer diagonalization and a least-squares-fitting routine. The results are presented in Table I. In this analysis it was assumed that the z axes of the $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ tensors coincide with each other and with the symmetry axis z of the Pb^{+} center. This could be an approximation.

B. Motional effects

When the ESR spectra are studied as a function of temperature, subtle but significant changes are observed. The two $\theta=45°$ lines in Fig. 1 broaden above 10 K and as the temperature is raised they average into a single line at about 32 K (see Fig. 3). This behavior clearly indicates that a limited motion is taking place within the Pb^{+} center, which is such that the small tipping effect with respect to $\langle 100\rangle$ is averaged out. This must be either a librational motion with respect to a $\langle 100\rangle$ direction in a $\{110\}$ plane, or a pyramidal motion[22] around $\langle 100\rangle$.

At about 64 K it becomes clear that the Pb^{+} ESR spectrum possesses a small orthorhombic component. Figure 4 shows the two $\theta=90°$ lines of the even-A Pb spectrum observed when $\vec{H}\,||\,\langle 110\rangle$. These two lines define g_x and g_y with $x\,||\,[1\bar{1}0]$ and $y\,||\,[110]$. Figure 5 presents the corresponding highest $\theta=90°$ hf line of ^{207}Pb, also distinctly showing the splitting due to the small orthorhombic component. The anisotropy of the low-field hf lines around 0.23 mT is so small that no orthorhombic splitting is observable there. The results of the ESR analysis at 32 and 64 K are included in Table I. A distinct reduction of the hf components with increasing temperature is observed. Finally, a pulse anneal (Fig. 6) establishes that the Pb^{+} center decays thermally around 160 K in KCl and the same decay temperature is found in RbCl.

IV. IDENTIFICATION AS $Pb^{+}(6p^{1})$

The ESR parameters (Table I) leave no doubt that one is dealing essentially with a $Pb^{+}(6p^{1})$ species. The large negative shifts of the g components and their relative magnitude ($g_{\parallel}>g_{\perp}$) are similar to those observed for the Tl^{0} defects.[7–9] They are characteristic for a single p electron and their magnitude reflects the large spin-orbit-coupling constants of these heavy metal ions $[\lambda(Pb^{+})\approx 9.400\ \mathrm{cm}^{-1}]$.

The hf components exhibit the property that $|A_{\perp}|>|A_{\parallel}|$. Such behavior is typical for the np^{1} ($n=4,5,6$) atoms and ions situated in a crystal field possessing reflection symmetry in a plane perpendicular to

TABLE I. Spin-Hamiltonian parameters of the $Pb^+(Cl_i^-)$ center in KCl and RbCl at various temperatures. Precision is ±0.001 for the g components and ±0.3 mT for the hyperfine components.

Crystal	Temp. (K)	g_z [a]	g_x	g_y	A_z [a]	A_x	A_y	Tipping angle θ_t	ΔH (mT)
$KCl:Pb^{2+}$	10	1.632	1.331		+ 163.5	−256.8		2.5°±0.1°	
	32	1.637	1.344		+ 160.8	−260.7	−247.3	a	6.0[b]
	65	1.636	1.340	1.357	+ 159.5	−257.2	−266.2	a	±2.0
$RbCl:Pb^{2+}$	10	1.609	1.276		+ 167.1	−263.5		7.0°±0.2°	
	32	1.607	1.283		+ 164.7	−259.7	−262.9	a	7.0
	65	1.610	1.288		+ 163.1	−252.7	−266.2	a	±1.0

[a] At $T=9$ K $\hat{z}\|[\langle 001\rangle+\theta_t$ in a $\{110\}$ plane]. Above 32 K tipping effects are averaged out and $\hat{z}\|[001]$, $\hat{x}\|[1\bar{1}0]$, and $\hat{y}\|[110]$.
[b] Linewidth ΔH is anisotropic in KCl and varies from 4.5±0.5 mT for $\theta=0°$ to 7.0±1.5 mT for $\theta=90°$. There is a small reduction in ΔH ($\sim 10\%$) when the temperature is raised improving the resolution.

the symmetry axis z.[3,7–9] In fact, for all these np^1 centers it has been established that $A_\perp < 0$ and $A_\| > 0$ and as a result the isotropic part A_σ of the hf components is found to be large and negative. Such a sign assignment also holds for the $Pb^+(6p^1)$ center (see Table I): It is the only sign combination yielding a physically acceptable magnitude for the anisotropic part

$$\rho=\frac{2}{5}\frac{\mu_I}{I}\langle r^{-3}\rangle \tag{2}$$

of the hf components. In Eq. (2), $\mu_I=0.5837$ nuclear magneton is the magnetic moment of the ^{207}Pb nuclear spin and $\langle r^{-3}\rangle$ is calculated over the $6p$ orbital of Pb^+.

Applying the approximate procedure of Ref. 3 and including second-order corrections to the hf components one deduces from $A_\|$ and $A_\perp$ (Table I) that very approximately,

$$A_\sigma \approx -45 ,$$

in mT, and

$$\rho \approx 34 ,$$

also in mT. This confirms a property that is a common characteristic of the heavy np_1 atoms and ions ($n=4,5,6$), namely, that the isotropic contribution to the hf interaction is in all cases large and negative.[3,7–9] This property holds for atoms and ions in the free state or in crystal fields possessing inversion symmetry. In the latter case no s mixing can occur in the np orbital which, if sufficiently strong, could yield positive A_σ values. In fact, for the so-called laser-active $Tl^0(1)$, $In^0(1)$, and $Ga^0(1)$ centers[3,7–9] in strong odd fields, positive A_σ values are indeed observed.

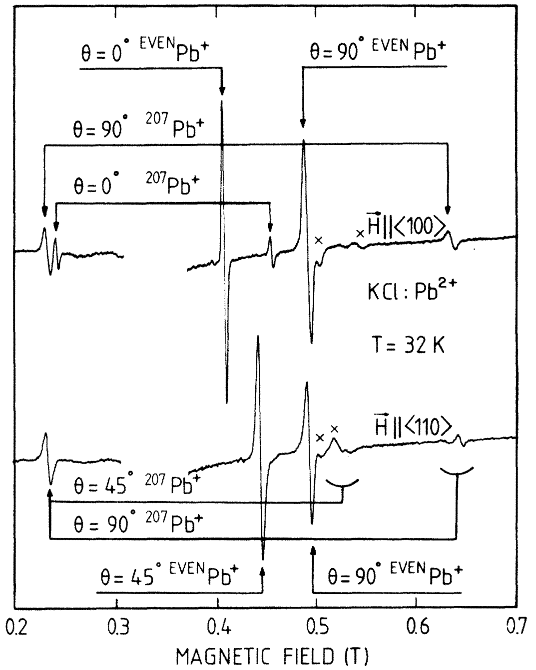

FIG. 3. $Pb^+(Cl_i^-)$ ESR spectra in $KCl:Pb^{2+}$ taken at 32 K. Splitting of the $\theta=45°$ in Fig. 1 has disappeared here because of a rapid librational motion.

V. MODEL FOR THE Pb^+ CENTER

In proposing a model for the Pb^+ center described in this paper one should take into account the following ob-

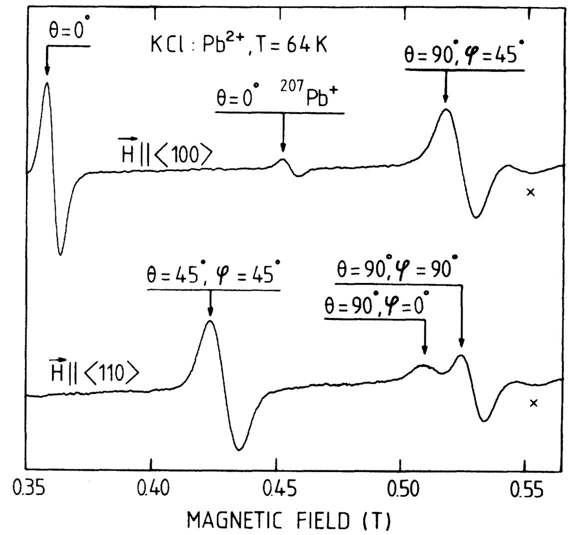

FIG. 4. $Pb^+(Cl_i^-)$ ESR spectra in $KCl:Pb^{2+}$ taken at 64 K and clearly showing the orthorhombic character of the g components in the two $\theta=90°$ spectra observed for $\vec{H}\|\langle 110\rangle$. They coalesce into a single line for $\vec{H}\|\langle 100\rangle$.

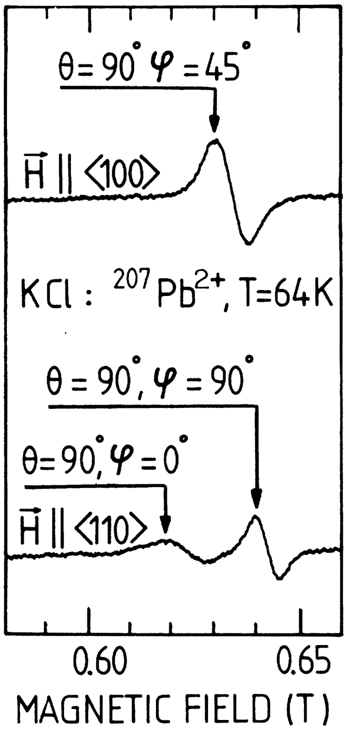

FIG. 5. High-field hf lines of the $^{207}Pb^{+}(Cl_i^{-})$ ESR spectra in 92% enriched KCl:$^{207}Pb^{2+}$ clearly showing the orthorhombic character of the hf components in the $\vec{H}||\langle 110\rangle$ spectrum. Again they coalesce into a single line for $\vec{H}||\langle 100\rangle$.

servations which were discussed in the foregoing sections.

(i) It takes a long x-ray irradiation at low temperatures (77 K), typically a few hours, to obtain a reasonable concentration of these Pb^{+} centers.

(ii) The center possesses to a good approximation axial symmetry around the z axis.

(iii) At low temperatures (~ 10 K) the symmetry axis z is tipped away from a $\langle 001\rangle$ direction in a $\{110\}$ plane by a small angle.

(iv) At higher temperatures a liberational motion of the Pb^{+} takes place which averages out the tipping but leaves the center with a small orthorhombic symmetry component.

(v) The behavior of the hf components suggests that the Pb^{+} center possesses either exactly or to a good approximation a reflection plane perpendicular to the symmetry axis z.

The first observation is important. The primary Pb^{+} centers which are strongly produced by simple electron trapping by the Pb^{2+}-cation vacancy complexes are formed very rapidly at 77 K, typically within 5–10 min with our x-ray source. These primary centers have not been observed in X-band ESR. The long irradiation times necessary for the production of our Pb^{+} center strongly point to the fact that an interstitial halogen ion is involved in its structure. These interstitials are mobile above 35 K, whereas the anion vacancies produced at the same time are immobile up to 220 K.[7] Thus it is unlikely that anion vacancies are part of the defect structure.

The fifth observation suggests in analogy with the primary $SnCl_2^{-}$,[1] $GaCl_2^{2-}$, and $InCl_2^{2-}$ centers[3,8] that the $6p_z$ orbital of the Pb^{+} forms molecular bonds with two adjoining Cl^{-} ions which are either exactly or nearly equivalent. The superhyperfine interaction with the $I=\frac{3}{2}$ chlorine nuclei is, however, not resolved in the rather broad linewidth.

The model that we propose and that is in agreement with the foregoing facts and considerations is presented in Fig. 7: A substitutional Pb^{+} is perturbed by an interstitial chloride ion, Cl_i^{-}, in the neighborhood. The Pb^{+} has molecular bonds with the two adjoining substitutional Cl^{-} ions nos. 1 and 2 forming a $PbCl_2^{-}$ molecular ion possessing approximately reflection symmetry with respect to a plane perpendicular to the molecular axis z. The Cl_i^{-} no. 3 ion in the nearest tetrahedral interstitial position perturbs the $PbCl_2^{-}$ tilting it away from [001] in a $\{110\}$ plane. We shall name this center $Pb^{+}(Cl_i^{-})$.

This model permits the following librational motion which explains the averaging out of the tipping effects in the ESR spectra: The Pb^{+} while maintaining its one bond with Cl^{-} no. 1 ion switches its other bond back and forth between Cl^{-} ions nos. 2 and 3. These ions jump alternatively into their nearest accessible interstitial tetrahedral

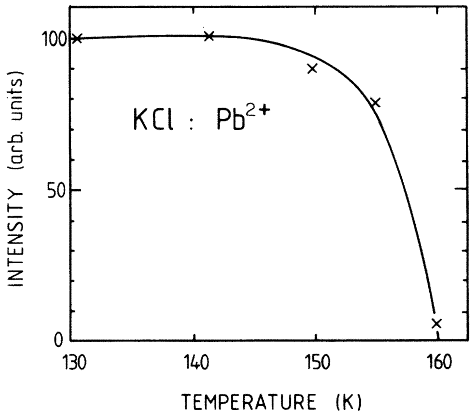

FIG. 6. Pulse-anneal data on the $Pb^{+}(Cl_i^{-})$ center in KCl showing its thermal decay. Results for RbCl are virtually identical.

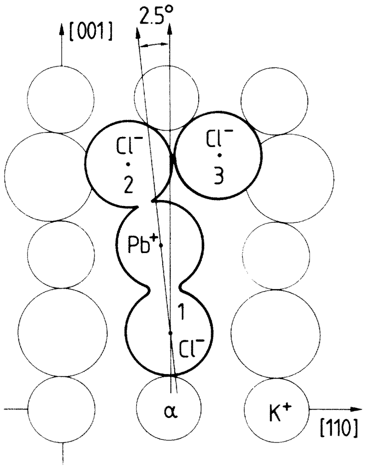

FIG. 7. Schematic model in a $\{110\}$ plane of the $Pb^{+}(Cl_i^{-})$ center in KCl as derived from the ESR spectra taken at 9 K. Center can librate with respect to the [001] direction in the $(1\bar{1}0)$ plane of the figure.

sites. This motion results in the averaged configuration schematically illustrated in Fig. 8.

The proposed $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ model in Fig. 7 is negatively charged with respect to the lattice. From a symmetry point of view it is still possible that alkali ion α in Fig. 7 is replaced by a positive-ion vacancy. However, this would make the center doubly negatively charged. Such a model is less appealing: The Cl_i^{-} and the cation vacancy repel each other and one may wonder why they would want to associate within the same defect structure.

VI. PRODUCTION OF THE $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ CENTER

A. Production by x-ray irradiation

The $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center of Fig. 7 is probably produced as follows. Before x-ray irradiation, but after the routine quenching to room temperature from about 700 K, the Pb^{2+}-doped KCl and RbCl samples possess substitutional Pb^{2+} ions associated with a charge-compensating cation vacancy either in a NN position along $\langle 100 \rangle$ and/or in a NNN position along $\langle 100 \rangle$. These are undoubtedly the dominant defects, but what their relative concentrations are is not known[23] and is not important here. However, it is also possible that a small amount of locally uncompensated Pb^{2+} is present. Mobile electrons produced at 77 K are rapidly trapped by these three types of Pb^{2+} defects forming the three possible primary $\mathrm{Pb}^{+}(6p^{1})$ defects. These are not observed in *X*-band ESR possibly because of rapid reorientation motions.[3]

In principle the primary Pb^{+} centers can now trap mobile Cl_i^{-}. Compared to electrons (and holes) the Cl_i^{-} are produced at a much slower rate by the x-ray irradiation. However, the dominant primary Pb^{+} centers associated with a cation vacancy are negatively charged and are repulsive for the mobile Cl_i^{-}. This is not so for the third unperturbed primary Pb^{+} and this one is more likely to stabilize a mobile Cl_i^{-} in the manner indicated in Fig. 7. In case it would be established that virtually no unperturbed Pb^{+} exists, one could argue that a mobile Cl_i^{-} is able to repel with some probability the cation vacancy away from the Pb^{+} while it is subsequently trapped by the unperturbed Pb^{+} center which is left behind.

B. Effect of *F*-center bleach

An optical excitation of the *F* centers (540 nm) at low temperatures, which results in the release of mobile electrons, has no noticeable effect on the $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center concentration. However, it has an effect on the concentration in the following experiment. If the sample containing the $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center is first warmed into the temperature region where the center decays (>150 K) and then is cooled again, one may recover virtually all the lost $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ centers by an optical excitation of the *F* centers. Presumably the $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center decays by losing its trapped electron forming the Pb^{2+}-Cl_i^{-} complex, called the precursor center. This process remains possible as long as the sample is not warmed above 210 K. One must conclude that above 200 K the trapped Cl_i^{-} breaks away from the Pb^{2+}. It is probably not accidental that interstitial chlorine atoms Cl_i^{0} trapped by divalent cations become untrapped in a comparable temperature region, i.e., around 230 K.[20]

The Pb^{2+}-Cl_i^{-} precursor center can be produced directly by x-ray irradiation in the (150–230)-K temperature range. This is illustrated by the following experiment. A KCl:Pb^{2+} sample is x-ray irradiated for 10 min at a temperature between 150 and 230 K, a region in which no $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ centers are produced. If this sample is then excited at low temperatures (77 K) in the *F* band the $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ is strongly produced. The data are presented in Fig. 9. This experiment does not work above 230 K implying that there the Pb^{2+}-Cl_i^{-} precursor center is not stable any longer.

VII. CONCLUDING REMARKS

The $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center discussed in this paper is but one of the many Pb^{+}-type defects that can be produced by x-ray irradiation in Pb^{2+}-doped alkali halides.[4] The ESR spectra of the several Pb^{+} centers produced above 220 K

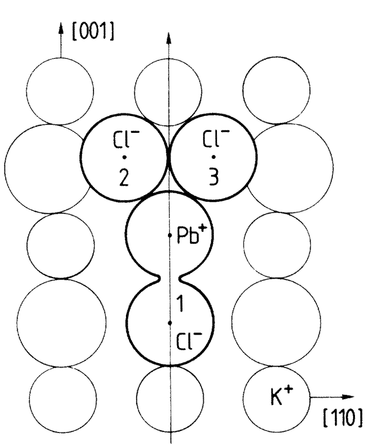

FIG. 8. Librationally averaged $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ structure as derived from the ESR measurements above 32 K. Interstitial character is now shared equally by Cl^{-} ions nos. 2 and 3.

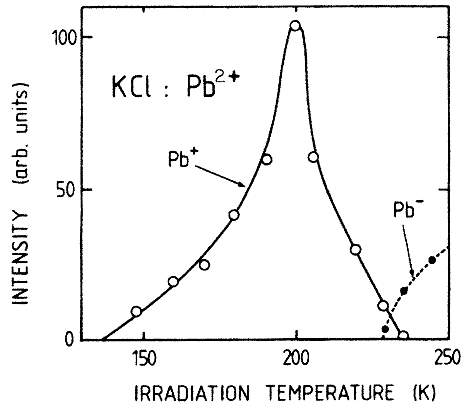

FIG. 9. Production of the $\mathrm{Pb}^{+}(\mathrm{Cl}_i^{-})$ center by an x-ray irradiation at the temperatures indicated in the figure followed by an optical *F*-center excitation at 77 K. Experiment implies that a Pb^{2+}-Cl_i^{-} precursor center is produced by the x-ray irradiation.

(where anion vacancies are mobile) overlap each other strongly and this together with the presence of the various Pb^- ESR spectra[5] makes their unraveling quite difficult. The fact that the $Pb^+(Cl_i^-)$ ESR spectra are so readily isolated and analyzed has two reasons: First it is produced at 77 K where anion vacancies are immobile, and second the primary Pb^+ centers, of which there are very likely three which are rapidly produced by simple electron trapping, are not observed at X-band frequencies. The model that we propose for $Pb^+(Cl_i^-)$ is the simplest one that we can think of that is in agreement with the experimental observations set forth in Sec. V. With regard to the $Pb^+(6p^1)$ hyperfine interaction we have now firmly established that the electron-spin density at the nuclei of the np^1 ($n=4,5,6$) atoms and ions is negative. This has been shown to be the case for Pb^+ in this paper and for $Tl^0(6p^1)$, $In^0(5p^1)$, and $Ga^0(4p^1)$ in Refs. 3,7–9, and 15. A forthcoming analysis of the $Sn^+(5p^1)$ hf interaction will fully confirm this.[24]

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