Electron-spin-resonance study of Pb2 3+ dimer centers in NaCl:PbCl2
Heynderickx, I.E.J.; Goovaerts, E.; Schoemaker, D.

Published in:
Physical Review B: Condensed Matter

DOI:
10.1103/PhysRevB.36.1843

Published: 01/01/1987

Citation for published version (APA):
Electron-spin-resonance study of Pb$^{3+}$ dimer centers in NaCl:PbCl$_2$

I. Heynderickx, E. Goovaerts, and D. Schoemaker

Physics Department, University of Antwerp (Universitaire Instelling Antwerpen),
B-2610 Wilrijk-Antwerpen, Belgium

(Received 8 December 1986)

A quantitative analysis is presented for the electron-spin-resonance spectra of five new defects, which are produced in NaCl:PbCl$_2$ samples by an x irradiation at 77 K and eventual thermal anneal to higher temperatures. The symmetry which is near to orthorhombic along, e.g., [100],[001],[110] axes, and the resolved hyperfine structure lead for all these defects to a model consisting essentially of a trapped electron Pb$^{3+}$ lead dimer center. A quantitative analysis is performed on the g components and the hyperfine interaction in terms of the molecular structure. The absence of Pb$^{3+}$ defects in KCl:PbCl$_2$ samples indirectly demonstrates the different aggregation behavior of divalent impurity-cation vacancy dipoles in both hosts.

I. INTRODUCTION

Spectroscopic techniques such as optical absorption, luminescence excitation transfer, Raman scattering, ionic thermocurrent, and electron spin resonance (ESR) are widely used to monitor the aggregation and precipitation of divalent ion-cation vacancy (IV) dipoles in alkali halides. Many of these studies have been performed on crystals doped with the paramagnetic Mn$^{2+}$ (Refs. 2-4) and the diamagnetic Pb$^{2+}$ (Refs. 5-8) ions. The aggregation of impurities which are not optically visible, such as Ca$^{2+}$, Sr$^{2+}$, and Cd$^{2+}$, is often investigated by incorporating Pb$^{2+}$ ions as a second impurity in the crystals. Those spectroscopic results lead to a detailed description of two possible clustering mechanisms: either aggregation from trimers to pentamers, heptamers, etc. by adding each time one dimer, or precipitation to a Suzuki phase, the structure of which can be observed in x-ray diffraction.

Some years ago a comparative study on lead-doped KCl and NaCl crystals was undertaken in order to determine the kind of clustering in these samples. In the former, clusters consisting of trimers, pentamers, etc. are produced during the first stages of the aggregation mechanism and finally PbCl$_2$ precipitates are formed. In the latter only Suzuki phase precipitates develop after high-temperature (above 440 K) aging experiments. Moreover, it is demonstrated that the aggregation in NaCl proceeds considerably faster than in KCl. In the present paper this behavior is indirectly confirmed by comparing the results of an ESR study on NaCl:PbCl$_2$ crystals with those of KCl:PbCl$_2$ and RbCl:PbCl$_2$ crystals, discussed earlier.

When either a quenched KCl:PbCl$_2$ or RbCl:PbCl$_2$ crystal is x-irradiated at liquid-nitrogen temperature (LNT) or room temperature (RT), several paramagnetic defects are observed, which each essentially consist of a hole or one or several electrons trapped at an isolated Pb$^{2+}$-cation vacancy dipole. ESR studies on lead-doped KCl samples have revealed the characteristic structure of the trapped hole Pb$^{3+}$ defect and the trapped electron Pb$^{2+}$ (Cl$^{-}$) (Ref. 12), Pb$^{-}$ (Ref. 15) and Pb$^{+}(1)$ defects. The existence of the so-called primary trapped electron Pb$^{2+}(0)$ center has only been demonstrated in optical-absorption measurements. On the other hand, in lead-doped RbCl samples the Pb$^{2+}$ (Cl$^{-}$) defect and the so-called Pb$^{+}(1)$ defects were studied together with their counterparts in KCl, but until now no results have been reported about the Pb$^{2+}(0)$, Pb$^{-}$, or Pb$^{+}(1)$ defects.

Optical absorption of the primary trapped electron Pb$^{2+}(0)$ center has also been observed in quenched and x-irradiated NaCl:PbCl$_2$ crystals. Our ESR results on such samples, however, mainly show the presence of defects consisting essentially of an electron trapped by a dimer of Pb$^{2+}$ ions. Consequently, these centers will be called "Pb$^{2+}$ centers." Similar dimer defects have been studied in heavily doped KCl:TCI crystals, namely, the so-called Tl$^{+}$ (110) (Ref. 17) and Tl$^{2+}$ (111) (Ref. 18) centers. The former, produced by a short x irradiation at 77 K, consists of an electron, trapped by two adjacent substitutional Tl$^{+}$ ions and as a result, the molecule is directed along a ⟨110⟩ axis. The proposed model for the latter, which is quite easily produced by an x-irradiation at temperatures above 220 K, consists of a Tl$^{2+}$ molecule ion on a single cation site which is oriented along a ⟨111⟩ direction.

In Sec. II we present the analysis of the ESR spectra of the Pb$^{2+}$ centers in NaCl:PbCl$_2$ crystals. The influence of the presence of oxygen impurities on the detailed defect structure is checked by comparing the spectra of NaCl crystals, to which 0.1 mol % PbCl$_2$ was added in the melt and which were grown by the Kyropoulos method in air, to those of NaCl crystals, to which 0.2 mol % PbCl$_2$ was added and which were grown by the Bridgman-Stockbarger method in a reactive atmosphere. The hyperfine (hf) interaction of the paramagnetic electron with the $^{207}$Pb nuclei was measured in an oxygen-free NaCl crystal, which was grown from a melt containing 0.13 mol % of the 92% enriched $^{207}$PbCl$_2$. Section III contains some typical production properties of the Pb$^{2+}$ defects. In Sec. IV we discuss the proposed model for the essential core of the structure of those defects.
II. QUANTITATIVE ANALYSIS

A. Determination of the g tensor

X irradiation of a quenched NaCl:PbCl$_2$ sample at LNT and a subsequent pulse anneal to a temperature between LNT and RT generates, apart from the spectrum of the $V_z$ center and the Pb$^{2+}$ defect, a number of resonance lines which are attributed to Pb-associated defects (Figs. 1 and 2). The spectra are all recorded at 15 K and at a microwave power of 100 mW. The angular dependence of the resonance spectra observed for a rotation of the static magnetic field $\mathbf{H}$ in a (100) plane of the crystal shows a symmetry close to orthorhombic along a set of $(x,y,z)$ axes being, e.g., [(110), [001], [110]]. We will designate the resonance lines by their polar angles $\theta$ and $\phi$, describing the orientation of $\mathbf{H}$ with respect to these $(x,y,z)$ axes.

According to the natural abundance of 79% for the even Pb isotopes without nuclear spin ($I=0$), the dominant contribution to the ESR lines of a NaCl:PbCl$_2$ crystal originates from paramagnetic electrons interacting with even Pb nuclei. Consequently, for such species the principal values of the g tensor along the $(x,y,z)$ axes are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)

The g parameters, resulting from an analysis of the spectra (Figs. 1 and 2) measured after a specific thermal anneal, are obtained by describing the resonance lines in terms of a spin Hamiltonian, containing only the Zeeman interaction for a value of the electron spin $S = \frac{1}{2}$ (usual notation):

$$\frac{\mathbf{H}}{g\mu_B} = \frac{1}{g_0} \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}.$$  

(1)
nealing treatment (Sec. III) are given in Table I. There, the different centers are enumerated in parentheses by a roman numeral.

Characteristic for all these centers is the large anisotropy in the \((x,y)\) plane: the \(g_x\) is almost equal to the mean value of \(g_y\) and \(g_z\). In Fig. 3 the angular dependence for rotation in a \((100)\) plane is shown for the \(\text{Pb}^{2+}\) (III) defect, described by \(g\) values which exactly obey the relation \(g_2^2 = \frac{1}{2}(g_x^2 + g_y^2)\). This modifies the picture for an angular variation in a \((100)\) plane in the case of orthorhombic symmetry along \((110)\) axes so that the \((\theta = 45^\circ, \phi = 0^\circ)\) resonance line becomes accidentally degenerate with the \((\theta = 90^\circ, \phi = 90^\circ)\) line.

For three \(\text{Pb}^{2+}\) defects the \(z\) axis of the \(g\) tensor is tilted away from the \([110]\) axis in the \((110)\) plane over an angle \(\gamma\), given in Table I. The presence of such a tilting is demonstrated by a shift of the \((\theta = 90^\circ, \phi = 90^\circ)\) resonance line and a splitting of the \((\theta = 60^\circ, \phi = 54.7^\circ)\) resonance line. The latter is illustrated in Fig. 1 for the \(\text{Pb}^{2+}\) (II) center and in Fig. 4 for the \(\text{Pb}^{2+}\) (IV) defect. These effects were not observed for the remaining defects mentioned in Table I, and because of the experimental linewidth of about \(8 \text{ mT}\) for the resonance lines we can conclude that if a tipping angle is present, it will be smaller than \(2.5^\circ\).

B. Determination of the hyperfine tensor

In the ESR spectra or NaCl crystals, enriched with the \(^{207}\text{Pb}^{2+}\) isotope with nuclear spin \(I = \frac{1}{2}\), one observes for each of the defects a splitting of the \(I = 0\) resonance line into four lines of nearly equal intensity (Fig. 2). Such a hyperfine structure is characteristic for the interaction of an \(S = \frac{1}{2}\) electron spin with two \(I = \frac{1}{2}\) nuclear spins. One of the lines, however, is situated within the experimentally measured linewidth at the same magnetic field position as the analyzed \(I = 0\) line (Sec. II A). This is only possible in the case of two nearly equivalent \(I = \frac{1}{2}\) nuclei, for which the nuclear spins \(I\) combine in a good approximation to a total nuclear spin \(I (I = 0, 1)\). The splitting into \(four\) lines is now explained by the assumption of \(hf\) terms which are sufficiently large compared to the Zeeman energy.

The principal values of the \(A\) tensor, which describes this interaction, are obtained by fitting the experimental data to the spectra predicted by the spin Hamiltonian

\[
\mathbf{H}_{\text{spin}} = g \mu_B \mathbf{B} \cdot \mathbf{S} + A \mathbf{I} \cdot \mathbf{S}
\]

where \(g\) is the electron's Landé g-factor, \(\mu_B\) is the Bohr magneton, \(\mathbf{B}\) is the external magnetic field, \(A\) is the hyperfine constant, and \(\mathbf{I}\) is the nuclear spin operator. The \(A\) tensor is diagonal in the crystallographic axes, and its principal values \(A_x, A_y, A_z\) are given in Table I. The accuracy of the measurements is typically \(0.002 \text{ cm}^{-1}\) on the principal axis, \(0.01 \text{ cm}^{-1}\) on the other two axes.

### Table I

<table>
<thead>
<tr>
<th>Defect</th>
<th>(g_x)</th>
<th>(g_y)</th>
<th>(g_z)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pb}^{2+}) (I)</td>
<td>1.222</td>
<td>1.438</td>
<td>1.625</td>
<td>0</td>
</tr>
<tr>
<td>(\text{Pb}^{2+}) (II)</td>
<td>1.188</td>
<td>1.479</td>
<td>1.537</td>
<td>6.7</td>
</tr>
<tr>
<td>(\text{Pb}^{2+}) (III)</td>
<td>1.300</td>
<td>1.469</td>
<td>1.621</td>
<td>0</td>
</tr>
<tr>
<td>(\text{Pb}^{2+}) (IV)</td>
<td>1.231</td>
<td>1.462</td>
<td>1.638</td>
<td>16.4</td>
</tr>
<tr>
<td>(\text{Pb}^{2+}) (V)</td>
<td>1.237</td>
<td>1.428</td>
<td>1.597</td>
<td>4.2</td>
</tr>
</tbody>
</table>

### Figure 3

The angular variation of the ESR spectra for the \(\text{Pb}^{2+}\) (III) defect in NaCl: PbCl\(_2\) is given for a rotation of the external magnetic field \(\mathbf{H}\) in a \((100)\) plane of the crystal. The experimental results, represented by the dots, are compared with the solid lines, showing the theoretically calculated angular dependence.

### Figure 4

The ESR lines \((\nu = 9.28 \text{ GHz})\) of the \(\text{Pb}^{2+}\) (IV) defect in NaCl doped with \(\text{Pb}^{2+}\) according to its natural isotope abundance, are shown for an external magnetic field \(\mathbf{H}\) along \((100)\) and \((110)\) crystallographic axes \((T = 15 \text{ K})\). The lines denoted by \(\text{even}\text{Pb}^{2+}\) (IV) involve two \(\text{even}\text{Pb}\) nuclei, while those denoted by \([\text{Pb}^{2+}]_{\text{doublet}}\) involve one \(\text{even}\text{Pb}\) and one \(^{207}\text{Pb}\) nucleus.
(usual notation):

$$\frac{\mathcal{H}}{g_0 \mu_B} = \frac{1}{g_0} H \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I},$$

(2)

with $S = \frac{1}{2}$ and $I = 0, 1$, and in which the $g$ values of Table I are substituted. This fitting was performed using the so-called "simulated-anneal" method, which is a recently developed minimization procedure based on the Metropolis Monte Carlo algorithm. The results of this analysis, in which it is assumed that the principal axes of the $A$ tensor coincide with the principal axes of the $g$ tensor, are given for the $\text{Pb}^{2+}(\text{I}), \text{Pb}^{2+}(\text{III}), \text{Pb}^{2+}(\text{IV})$, and $\text{Pb}^{2+}(\text{V})$ centers in Table II. In contrast to the large anisotropy in the $g$ values, the $A$ parameters are nearly isotropic. Consequently, the hf lines exhibit qualitatively the same angular dependence of the magnetic field for rotation in the $z$ plane as the $I = 0$ resonance lines.

For a NaCl crystal, doped with $\text{Pb}^{2+}$ ions according to their natural abundance of isotopes, i.e., 79% of the even${}^{207}\text{Pb}$ nuclei with $I_i = 0$ and 21% of the odd${}^{209}\text{Pb}$ nuclei with $I_i = \frac{1}{2}$, one can determine the expected intensity for each of the possible combinations of the isotopes in the $\text{Pb}^{2+}$ dimer. The even${}^{207}\text{Pb}$-odd${}^{209}\text{Pb}$ combination occurs for 62% and causes no splitting of the resonance lines. The even${}^{207}\text{Pb}$-odd${}^{209}\text{Pb}$ combination has an abundance of 34% and because of its doublet structure each of the resonance lines will reach an intensity of 17%. The odd${}^{207}\text{Pb}$-odd${}^{209}\text{Pb}$ combination occurs for only 4% and because of the corresponding quartet structure the lines will have a negligible intensity of 1%. For the $\text{Pb}^{2+}(\text{IV})$ defect the doublet structure of the electron interacting with a $\text{Pb}^{2+}$ nucleus and a even${}^{207}\text{Pb}$ nucleus is shown in Fig. 4.

For the $\text{Pb}^{2+}(\text{II})$ defect the resonance lines in our NaCl${}^{207}\text{PbCl}_2$ samples were absent for an unknown reason. In principle, however, the $A$ values can now be determined from the doublet structure, which is detected in NaCl${}^{207}\text{PbCl}_2$ samples, doped with $\text{Pb}^{2+}$ ions according to their natural abundance. Because of the simultaneous occurrence of the $\text{Pb}^{2+}(\text{I})$ defect with the $\text{Pb}^{2+}(\text{II})$ defect, a sufficiently accurate identification of the resonance lines, and as a consequence an analysis of the hf interaction, was made impossible for the latter defect.

### Discussion of the $g$ Tensor

Since the $\text{Pb}^{2+}$ dimer center consists of a single valence electron trapped by two $6s^2 \text{Pb}^{2+}$ ions, its electronic configuration is equal to one of the $T1_2^-$ centers and complementary to that of the $V_k$ center. The molecular $g$ ground orbital, which is considered as a linear combination of the atomic orbitals, namely

$$g = \alpha_2(6s_1 + 6s_2) + \beta_2(6p_{x,1} - 6p_{x,2}),$$

is singly occupied. The excited $\pi^* = \mu_2(6p_{x,1} - 6p_{x,2})$ and $\pi^* = \mu_2(6p_{y,1} - 6p_{y,2})$ orbitals, separated from the ground state by an energy $E_{1g}$ and $E_{2g}$, respectively, are mixed into $g$ by spin-orbit interaction. Their energy values can be determined from the experimentally measured $g$ shifts by a perturbation calculation, pushed to second order with spin-orbit coupling as perturbation. The complete expressions for a $\text{Pb}^{2+}$ center in an orthorhombic crystal field are given by

### Table II. The hyperfine components, the anisotropic part $\rho_s$, and isotropic part $A_s$ of the hyperfine interaction are given in units of mT for the $\text{Pb}^{2+}$ centers in NaCl${}^{207}\text{PbCl}_2$. Signs of the hyperfine components are attributed according to the constraint of a positive and constant $g$ value. Errors are estimated to be 1 mT.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$A_s$</th>
<th>$A_s$</th>
<th>$A_s$</th>
<th>$\rho_s$</th>
<th>$A_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pb}^{2+}(\text{I})$</td>
<td>-117</td>
<td>-122</td>
<td>+125</td>
<td>+47</td>
<td>-17</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(\text{III})$</td>
<td>-115</td>
<td>-123</td>
<td>+115</td>
<td>+48</td>
<td>-23</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(\text{IV})$</td>
<td>-121</td>
<td>-120</td>
<td>+123</td>
<td>+48</td>
<td>-18</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(\text{V})$</td>
<td>-114</td>
<td>-121</td>
<td>+126</td>
<td>+48</td>
<td>-17</td>
</tr>
</tbody>
</table>
\[
\Delta g' = g_0 - g_v = -2 \frac{a_1^2 \lambda_{g,k}}{E_{1g}} \delta_y + 2 \frac{b_1^2 \lambda_{g,k}}{E_{2g}} \delta_y - 2 \frac{a_1^2 \lambda_{g,k}}{E_{1g}} \delta_y + 2 \frac{b_1^2 \lambda_{g,k}}{E_{2g}} \delta_y + 2 \frac{a_2^2 \lambda_{g,k}}{E_{1g}} \delta_y + 2 \frac{b_2^2 \lambda_{g,k}}{E_{2g}} \delta_y + 2 \frac{a_1^2 b_2^2 \lambda_{g,k}}{E_{1g}} \delta_y + 2 \frac{b_1^2 b_2^2 \lambda_{g,k}}{E_{2g}} \delta_y + \frac{1}{2} \lambda_{g,k}^2 \left[ \frac{1}{E_{1g}} + \frac{1}{E_{2g}} \right] + a b \lambda_{g,k}^2 \left[ \frac{1}{E_{2g}} - \frac{1}{E_{1g}} \right].
\]

(3c)

In the second-order terms of these expressions the approximation \( \lambda_{g,k} = \lambda_{g,y} = \lambda_{g} \) is introduced, in which \( \lambda_{g,k} \) and \( \lambda_{g,y} \) are the matrix elements of the \( x \) and \( y \) component, respectively, of the orbital part of the spin-orbit coupling between the ground state and the excited states. The resulting \( \lambda_{g} \) and also the parameter \( \lambda_{g,y} \), which yields the expectation value of the \( z \) component of the orbital part of the spin-orbit coupling between the \( \pi_g \)'s, are given as a function of the molecular-orbital coefficients \( \mu_g \) and \( \beta_g \), and of the atomic spin-orbit-coupling constant \( \lambda > 0 \) by the relations

\[
\lambda_{g} = 2 \mu_g \beta_g \lambda , \quad (4a)
\]

\[
\lambda_{g,y} = 2 \mu_g^2 \lambda . \quad (4b)
\]

The numerical values for \( \mu_g \) and \( \beta_g \) are taken from Ref. 19. In order to reduce the number of unknown parameters in Eq. (3), the approximation \( \lambda_{g,k} = \lambda_{g,y} = \lambda_{g} \) is also extended to the first-order terms. In analogy to Ref. 17 we will approximate the \( \delta_i \) (\( i = x, y, z \)) values, which are the matrix elements of the corresponding component of the orbital-momentum operator in the Zeeman interaction, by the relation \( \delta_x = \delta_y = \delta \) and \( \delta_z = 0.8 \). The latter approximation was discussed in Ref. 17 and used here in order to have the possibility of comparing the results. The coefficients \( a \) and \( b \) in the excited states are given by

\[
a = k_g \lambda_{g,y} , \quad (5a)
\]

\[
b = k_g [ \Delta_g - (\Delta_g^2 + \lambda_{g,y}^2)^{1/2} ] , \quad (5b)
\]

in which \( k_g \) is the normalization constant such that \( a^2 + b^2 = 1 \). The crystal-field contribution \( \Delta_g \) can be expressed in terms of the energy difference by the zeroth-order relation:

\[
E_{2g} - E_{1g} = (\Delta_g^2 + \lambda_{g,y}^2)^{1/2} .
\]

(6)

For the \( \text{Tl}^{2+} \text{(110)} \) and \( \text{Pb}^{2+} \) defects the higher-order terms to (6) give a correction of less than 10%.

We want to remark that the expression (2) of Ref. 17 and (11) of Ref. 19 are incomplete as a consequence of an inconsistent approximation. But this does not influence the final results, since the axial approximation to the set of equations (3) yields the same expressions as those derived from the incomplete formulas of Refs. 17 and 19. In contrast to Ref. 17, however, the axial approximation in the description of the electronic structure is not applied here because of the large anisotropy between the \( g_x \) and \( g_y \) for all the \( \text{Pb}^{2+} \) defects. Consequently, a system of four nonlinear equations, of which three are given by the \( g \)-shift expressions (3) and the fourth by the normalization condition, has to be solved in terms of the parameters \( E_{1g}, E_{2g}, \delta, \) and \( k_g \). The influence of the axial approximation is investigated by comparing the solution of this problem for the \( \text{Tl}^{2+} \text{(110)} \) center\(^7\) and the \( \text{Pb}^{2+} \) center to the parameters \( E_{1g}, E_{2g}, \delta, \) and \( k_g \) obtained from the calculation procedure of Ref. 17 for \( \delta_z = 0.8 \). The data are listed in Table III.

It seems that for each of the defects the orthorhombic approach increases the values of \( \delta \) and lowers the excitation energies. As a result the orthorhombic description nearly reproduces the \( \delta \) value for the \( \text{Tl}^{2+} \text{(110)} \) center, which in Ref. 17 was theoretically estimated to be 0.67. The \( \delta \) value of the \( \text{Pb}^{2+} \) defect, however, is unreasonably small even in the orthorhombic approach.

### Table III. Comparison of \( \delta \), the normalization constant \( k_g \), and the excitation energies \( E_{1g} \) and \( E_{2g} \) in an axial approximation and in an orthorhombic description of the electronic structure for the \( \text{Tl}^{2+} \text{(110)} \) defect in KCl and the \( \text{Pb}^{2+} \text{((III))} \) defect in NaCl.

<table>
<thead>
<tr>
<th>Defect</th>
<th>( E_{1g} ) (eV)</th>
<th>( E_{2g} ) (eV)</th>
<th>( \delta )</th>
<th>( k_g ) (eV(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Tl}^{2+} \text{(110)} )(^a)</td>
<td>0.95</td>
<td>1.75</td>
<td>0.52</td>
<td>1.20</td>
</tr>
<tr>
<td>Axial</td>
<td>±0.05</td>
<td>±0.05</td>
<td>±0.03</td>
<td>±0.05</td>
</tr>
<tr>
<td>( \text{Tl}^{2+} \text{(110)} )(^a)</td>
<td>0.75</td>
<td>1.58</td>
<td>0.60</td>
<td>1.23</td>
</tr>
<tr>
<td>Axial</td>
<td>±0.01</td>
<td>±0.01</td>
<td>±0.01</td>
<td>±0.01</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} \text{((III))} )</td>
<td>1.00</td>
<td>2.95</td>
<td>0.20</td>
<td>0.70</td>
</tr>
<tr>
<td>Axial</td>
<td>±0.05</td>
<td>±0.05</td>
<td>±0.03</td>
<td>±0.05</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} \text{((III))} )</td>
<td>1.07</td>
<td>2.75</td>
<td>0.30</td>
<td>0.69</td>
</tr>
<tr>
<td>Axial</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.02</td>
<td>±0.02</td>
</tr>
</tbody>
</table>

\(^a\)Reference 17.
This can be seen from the approximate expression which allows an estimate of the interatomic distance \( R \):\(^{17}\)

\[
R = \frac{1 - \delta}{\alpha g \mu g \left| \frac{\partial}{\partial x} \left( 6x | \delta \right) \right| 6\rho_s}.
\]

Additional inaccuracy is introduced in this expression by the substitution of the approximate values of Ref. 19 for \( \alpha g, \mu g, \) and the gradient integral, the numerical value of which is unknown for a \( \text{Pb}_2^+ \) molecule. It results in a distance of 15 a.u., which we believe is much too large, mainly because of the small value of \( \delta \).

For the excitation energies of the \( \text{Tl}_2^+ (110) \) center a small discrepancy is found between the calculated energies and the detected optical-absorption bands, which are situated at 0.70 and 1.44 eV. However, we have to keep in mind that the \( \sigma_g \rightarrow \pi_g \) transitions are calculated, while optically the \( \sigma_g \rightarrow \pi_u \) transitions can be measured. For the \( \text{Pb}_2^+ \) defects, on the other hand, the positions of the absorption bands are still unknown and nothing can be concluded about the reliability of the high values of \( E_{\|g} \) and \( E_{\perp g} \). Consequently, it would be worthwhile to determine these positions, e.g., by the optically detected magnetic resonance (ODMR) technique, which allows one to directly connect the absorption bands to the ESR signals.

Finally, we want to note that a low accuracy was to be expected from this perturbative analysis because of the large spin-orbit-coupling constant: about a factor of 2 larger for the free \( \text{Pb}^+ \) ion \( (\lambda \approx 9400 \text{ cm}^{-1}) \) than for the free \( \text{Tl}^+ \) atom \( (\lambda \approx 5100 \text{ cm}^{-1}) \). Apart from the errors resulting from the application of the numerical values of Ref. 19 for some of the parameters, additional inaccuracy is introduced by describing the electronic structure of the \( \text{Pb}_2^+ \) defects on the basis of a one-electron, nonrelativistic, second-order perturbation calculation. Those deficiencies will be more important for heavy ions or atoms, possessing a high electron density at the nucleus and a large spin-orbit-coupling constant.

**D. Discussion of the hyperfine tensor**

The hf components for a diatomic molecule with a single valence electron in \( p_\sigma \) orbitals, characterized by a spin-orbit coupling \( \lambda \), in an axial approximation for the crystal field with energy \( E \), are given up to second order in \( \lambda/E \) in terms of the \( g \) shifts,

\[
\Delta g_1 = g_0 - g_1 = \frac{\lambda^2}{E},
\]

\[
\Delta g_1 = g_0 - g_1 = 2 \frac{\lambda^2}{E} + \frac{2 \lambda^2}{E^2},
\]

by the expression (for an extended discussion see Refs. 17 and 19)

\[
A_1(1 - \frac{1}{2} \Delta g_1) A_\sigma + (2 + \frac{1}{2} \Delta g_1 - 2 \Delta g_1) \rho_\sigma \frac{1}{2} \Delta g_1 \rho_\sigma,
\]

\[
A_1(1 - \frac{1}{2} \Delta g_1) A_\sigma - (1 + \frac{1}{2} \Delta g_1 + \frac{1}{2} \Delta g_1) \rho_\sigma,
\]

\[
- (\frac{1}{2} \Delta g_1 - \frac{1}{2} \Delta g_1) \rho_\sigma,
\]

in which \( A_\sigma = A_\sigma^\alpha + A_\sigma^\beta \) is the isotropic part, containing

\[
A_\sigma^\alpha = \frac{\mu_I}{I} \beta_{g}^2 (r^{-3})_g,
\]

the exchange polarization contribution;

\[
A_\sigma^\beta = \frac{8 \pi}{3} \frac{\mu_I}{I} \alpha_g^2 | \psi_g(0) |^2,
\]

the Fermi contact term;

\[
\rho_\sigma = \frac{2}{5} \frac{\mu_I}{I} \beta_{g}^2 (r^{-3})_g,
\]

the anisotropic part, describing the dipole-dipole interaction between the magnetic moments of the electron and nuclei; and

\[
\rho_\sigma = \frac{2}{5} \frac{\mu_I}{I} \beta_{g}^2 (r^{-3})_g,
\]

the anisotropic part, resulting from the interaction between the orbital moments of the electron and the nuclear moments. For many of the atomic and molecular systems it has been found that \( \rho_\sigma \approx 1.13 \rho_\sigma \) (Ref. 19).

In order to express the hf components as a function of the \( g \) shifts, we have introduced the approximation of axial symmetry. In the case of the \( \text{Pb}_2^+ \) centers, this is a crude approximation, which is, however, necessary because of the complexity of the relations to be applied for orthorhombic symmetry. Since \( \Delta g_1 \) and \( \Delta g_2 \) are known experimentally, one can calculate the values \( \rho_\sigma \) and \( A_\sigma \) of the hf interaction from the determination of the components \( A_1 \) and \( A_2 \). But in order to do so one needs the signs of \( A_1 \) and \( A_2 \), which cannot be obtained from the ESR spectra.\(^{21}\) They are assigned according to the imposed constraint of a constant \( \rho_\sigma \) value for the different \( \text{Pb}_2^+ \) defects, possessing the same sign as that of the magnetic moment of the Pb nucleus. For each of the defects the \( \rho_\sigma \) and \( A_\sigma \) value are included in Table II.

The calculation procedure in Ref. 17 illustrates that one can estimate the influence of surroundings and molecular structure on the hf interaction by comparing the experimentally determined \( \rho_\sigma \) and \( A_\sigma \) values with those obtained from a Hartree-Fock calculation of the \( 6p \) function of a free \( \text{Pb}^+ \) ion. Indeed, the ratio of the anisotropic hf term, \( \rho_\sigma \), of a given defect to that of the corresponding free atom or ion gives a measure of the delocalization of the ground orbital of the defect towards the surrounding lattice ions. And, the amount of \( s \) mixing into the ground orbital is determined from the difference of the experimentally measured \( A_\sigma \) value with that calculated for the free atom or ion, which contains exclusively the contribution of the exchange polarization, \( A_\sigma^\alpha \). In this calculation,\(^{17}\) however, the nonrelativistic limit is substituted in relativistic equations for the hf components. By doing so, errors are introduced, which become large for heavy atoms or ions possessing a high electron density at the nucleus. In particular when the calculation procedure is repeated for lead-associated defects, the results become unreasonable because of the importance of the neglected relativistic and correlation effects. Therefore we have attempted to get an idea of the delocalization and the \( s \) mixing by directly comparing the \( \rho_\sigma \) and \( A_\sigma \) values of the different \( \text{Pb}^+ \) defects, namely the \( \text{Pb}^+(\text{Cl}^-) \) defect in KCl, the \( \text{Pb}^+(1) \)
defect in KCl, and the Pb$_2^{3+}$(III) center in NaCl. The corresponding values are given in Table IV.

In our notation $\beta_k^2$ determines for a given Pb$^+$ defect the 6$p$ electron density around the nucleus of the Pb$^+$ ion, while the remaining density is distributed over the ligand ions. For a Pb$_2^{3+}$ defect the molecular wave function of the valence electron is spread over two Pb$^{2+}$ ions. Taking into account the overlap contribution $S_{pp}$ of the atomic 6$p$ orbitals in the molecular orbital, its electron density at the nucleus is proportional to $2\beta_k^2(1-S_{pp})$. The value of $S_{pp}$ is positive for a $\sigma_g$ ground orbital and estimated to be about 0.20. Consequently, one expects for the ratio of the $\rho_s$ values, i.e., the ratio of the $\beta_k^2$ values,

$$\frac{\beta_k^2[\text{Pb}_2^{3+}]}{\beta_k^2[\text{Pb}^+] = 2(1-S_{pp})^{-1} = 0.63.$$  

This value is surprisingly, but maybe fortuitously, well reproduced by the ratio of the experimentally determined $\rho_s$ values:

$$\frac{\rho_s[\text{Pb}_2^{3+}]}{\rho_s[\text{Pb}^+] = 0.63.$$  

The $A_\sigma$ value can now be determined from the experimentally measured $A_\sigma$ value on condition that the contribution of the exchange polarization, $A_e^x$, is known. The latter is estimated from the $A_\sigma$ value of the Pb$^{3+}$Cl$^-$ defect, for which the surrounding crystal field is believed to be essentially even and, consequently, little or no $A_e^x$ contribution is mixed into $A_\sigma$. So if we assume that no delocalization occurs for the Pb$^+$ defects, we find

$$\frac{\hbar}{I} \langle r^{-3} \rangle = -97 \text{ mT}.$$  

The $A_\sigma$ value is now given as $A_\sigma = -\beta_k^2(\mu_I/I)(r^{-3})_e$ and results in $A_\sigma = +40 \text{ mT}$ for the Pb$^{3+}$Cl$^-$ defect in KCl, and $A_\sigma = +37 \text{ mT}$ for the Pb$_2^{3+}$(III) defect in NaCl. The values of the other Pb$^+(1)$ and Pb$_2^{3+}$ defects are slightly different, reflecting the influence of the different crystalline environments. It demonstrates that for both kinds of defects $s$ mixing influences the isotropic part of the hyperfine interaction. For the Pb$^+(1)$ defects it originates from the odd component of the surrounding crystal field due to the presence of an anion vacancy along the [001] crystallographic axis. For the Pb$_2^{3+}$ center it results from the molecular bond.

### TABLE IV. The anisotropic part, $\rho_s$, and the isotropic part, $A_\sigma$, of the hyperfine interaction are compared for some Pb-associated defects (in units of mT). The estimated accuracy is 1 mT.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\rho_s$</th>
<th>$A_\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^+(\text{Cl}^-)$ in KCl$^a$</td>
<td>+76</td>
<td>-97</td>
</tr>
<tr>
<td>Pb$^+(1,a)$ in KCl$^b$</td>
<td>+74</td>
<td>-57</td>
</tr>
<tr>
<td>Pb$_2^{3+}$(III) in NaCl</td>
<td>+48</td>
<td>-23</td>
</tr>
</tbody>
</table>

$^a$Reference 13.

$^b$Reference 15.

**III. PRODUCTION PROPERTIES**

**A. Influence of quenching on the production**

As mentioned in the Introduction, IV dipoles in alkali halides tend to form aggregates and precipitates. These clusters can however be dissolved in the lattice by heating the crystals to temperatures near the melting point. The dissolved dipoles will be frozen in by quenching the samples as fast as possible to low temperatures, e.g., LNT. The NaCl:PbCl$_2$ crystals were handled in this way before the production of the Pb$_2^{3+}$ dimer centers by x irradiation. The influence of the annealing temperature and the rate of the quenching on the intensity of the ESR lines was studied for equal doses of x irradiation at LNT.

No difference in the concentration of the Pb$_2^{3+}$ centers is observed for samples which are annealed to temperatures between 770 and 920 K, on the condition that they are quenched at the same rate. An intensity decrease of about a factor of 2, however, results from cooling an annealed sample down to LNT within 20 min instead of within 2 min. Moreover, x-irradiating for 1 h a sample that was kept at RT for several months does not produce a detectable concentration of Pb$_2^{3+}$ centers. This suggests that they are produced from a dimer of IV dipoles, occurring during the first stage of the aggregation mechanism in NaCl:PbCl$_2$ crystals.

**B. Production by x irradiation at LNT as a function of time**

The intensity of the Pb$_2^{3+}$(II) defect in a quenched NaCl:PbCl$_2$ sample is given in Fig. 5 as a function of the time of x irradiation at LNT. It is normalized to its value for an x irradiation period of 100 min. The rate of formation of the Pb$_2^{3+}$ dimers is fast at the beginning of the irradiation, but decreases after about 15 min. The fast for-
mation during the first minutes of x irradiation would indicate that only simple processes such as hole or electron trapping are involved in the production of the centers. However, for such a production mechanism one usually finds a saturation in the concentration of the created defects. The relatively slow dropoff of the production rate, on the contrary, suggests the presence of additional time-consuming processes accompanying the hole and electron trapping. Since to our knowledge no interstitials or radiation-induced vacancies are involved in the Pb$_2$$^{3+}$ defect structure, the retarding effect on the production of the center should possibly be sought in the formation of a dimer configuration of nearest-neighboring Pb$^{2+}$ ions (see Sec. IV).

C. Pulse-anneal experiment after x irradiation at LNT

The temperature for maximal production of the Pb$_2$$^{3+}$ defects is examined in a pulse-anneal experiment. A quenched NaCl:PbCl$_2$ crystal is x-irradiated for 2 h at LNT and subsequently annealed for 2 min at temperatures between LNT and RT. The intensity, plotted in Fig. 6 as a function of the annealing temperature, was measured at $T = 15$ K as the mean value of the intensities of the different resonance lines belonging to the same defect. Nevertheless, we are dealing with a low accuracy on those results because of the overlap of resonance lines belonging to different centers.

Nevertheless, four stages can undoubtedly be recognized in the annealing curves. The Pb$_2$$^{3+}$(I) and Pb$_2$$^{3+}$(II) spectra have a maximal intensity immediately after x irradiation. The intensity of the Pb$_2$$^{3+}$(I) spectrum for higher annealing temperatures decreases slowly and becomes undetectable at about 180 K, while the concentration of the Pb$_2$$^{3+}$(II) defect decreases much faster and disappears at about 150 K. Meanwhile the Pb$_2$$^{3+}$(III) defect is produced and reaches a maximal amount at 150 K. The decrease in concentration of the latter at about 210 K is correlated with the production of the Pb$_2$$^{3+}$(IV) defect with a maximum concentration at 240 K. This center disappears at 260 K and the Pb$_2$$^{3+}$(V) center is formed with maximum concentration at 280 K. As can be checked from Fig. 6, the temperature range in which each of the defects occur becomes smaller for higher production temperatures. At the same temperature stages some other minor defects were present. They seem to show the same characteristics as the Pb$_2$$^{3+}$ defect; however, their intensity was too small to perform a quantitative analysis of their ESR spectra.

IV. DISCUSSION OF THE DEFECT STRUCTURE

As was already shown in the preceding sections, the essential core of all the centers, discussed in this paper, consists of an electron shared by two equivalent or nearly equivalent Pb$^{2+}$ ions and, consequently, the nomenclature of Pb$_2$$^{3+}$ centers was introduced. Since the Pb$^{2+}$ ions are substitutional in two neighboring cation sites, the molecular axis is directed along a $\langle 110 \rangle$ crystallographic axis. First, this kind of model is strongly suggested by the observed hf structure. Second, the model is consistent with the symmetry of the resonance spectra. Finally, the identification of the different resonance lines with Pb$_2$$^{3+}$ centers is supported by the production behavior of the centers under x irradiation and the need for quenching the crystal in order to disperse aggregates so as to obtain reasonable intensities of the centers.

Similar to the observation of many different “Pb$^{+}$” type” centers in lead-doped KCl and RbCl, several Pb$_2$$^{3+}$ centers, each showing the same essential features, are detected in NaCl:PbCl$_2$ crystals. In Refs. 13, 15, and 23-27 it was already suggested for divalent impurity ions like Pb$^{2+}$, Sn$^{2+}$, Mn$^{2+}$, and Fe$^{2+}$ that small variations in the model of a given defect originate from different positions for the charge-compensating cation vacancy with respect to this ion. Corresponding to the production temperature and the symmetry of the centers various positions for this vacancy were proposed in order to construct a possible model, such as, e.g., for the Pb$^{+}$ defects in KCl and RbCl.

The production temperature for each of the Pb$_2$$^{3+}$ centers (Sec. III C) demonstrates that small modifications in the neighborhood of the essential Pb$_2$$^{3+}$ structure occur as a result of higher annealing temperatures. It is still reasonable to attribute such changes in the crystal field experienced by the trapped electron dimer to displacements of the charge-compensating cation vacancies. But since, in principle, two cation vacancies are present in the environment of a lead dimer, many configurations can be constructed as possible models. This makes it impossible to suggest on the basis of the limited experimental results different models for each of the observed Pb$_2$$^{3+}$ centers. Moreover, it is not excluded that the crystalline environment is changed locally by additional impurity ions such as oxygen. In the specific case of the oxygen impurity, however, its influence can be excluded, since no difference is observed in the resonance spectra of oxygen-free and oxygen-containing NaCl:PbCl$_2$ samples. Finally, it is possible that the local neighborhood of the dimer center is disturbed by the presence of a third IV dipole. Such a proposal can be suggested on the basis of the aggregation process, described in Ref. 9 as the growth of a trimer.

FIG. 6. The results of a pulse anneal experiment in which a NaCl:PbCl$_2$ crystal is x-irradiated during 90 min at LNT and subsequently annealed during 5 min at temperatures between 130 K and RT, are shown: $\bigcirc$, Pb$_2$$^{3+}$(I); $\bigtimes$, Pb$_2$$^{3+}$(II); $\bullet$, Pb$_2$$^{3+}$(III); $\square$, Pb$_2$$^{3+}$(IV); $\triangle$, Pb$_2$$^{3+}$(V).
from a metastable dimer during the first stage of the clustering. 

An interesting result is the absence of Pb\textsuperscript{3+} centers in KCl:PbCl\textsubscript{2} crystals. Samples with various lead concentrations have been x-irradiated at LNT either as-grown or after a storage period at RT. Such a handling still resulted in a small concentration of the Pb\textsuperscript{3+} (Cl\textsuperscript{−}) defect. This confirms again that the clustering proceeds faster in NaCl:PbCl\textsubscript{2} than in KCl:PbCl\textsubscript{2}, in which almost no aggregation occurs during RT ageing.\textsuperscript{11} On the other hand, an explanation for the lack of Pb\textsuperscript{3+} centers in KCl can be found in the different type of IV dipoles, present in the two alkali halides. In Ref. 6 the results of polarized luminescence experiments are explained as indicating that in KCl the charge-compensating cation vacancy is almost exclusively situated at a next-nearest-neighbor (NNN) position of the Pb\textsuperscript{3+} ion, while in the NaCl it is also located in a nearest-neighbor (NN) position of the Pb\textsuperscript{3+} ion. During x irradiation one of the Pb\textsuperscript{3+} ions of a dimer or even a trimer, constructed from NN IV dipoles, can easily capture an electron and subsequently jump to an adjacent cation vacancy in order to produce Pb\textsuperscript{3+} centers, as observed in NaCl [Fig. 7(a)]. Such a mechanism, however, is impossible from dimers or trimers, constructed from NNN IV dipoles, since two Pb\textsuperscript{3+} ions never can reach next-neighboring positions by only interchanging their position with a cation vacancy [Fig. 7(b)]. This difference was already formulated more generally in Ref. 9. There, it is suggested that mainly NN IV dipoles tend to form aggregates starting from a trimer to which dimers are added. In the last stage of the clustering process, they ultimately precipitate by a total rearrangement of the IV dipoles. The NNN dipoles, on the contrary, for dimers in which the impurity ions are separated by more than two lattice sites and these dimers directly precipitate to the Suzuki phase, already extensively examined in KCl:PbCl\textsubscript{2} crystals.\textsuperscript{5} This behavior is also found in a theoretical calculation on the relative stability of various cluster configurations for different kinds of IV dipoles.\textsuperscript{28} Unfortunately, this work does not include the results for lead-doped alkali halides, but the tendency, reported from experiments on those crystals, is in agreement with the results obtained for other divalent ions.

**ACKNOWLEDGMENTS**

We are indebted to Dr. S. V. Nistor for his advice in the initial experiments and to Dr. A. Bouwen for his experimental assistance. The IIKW (Interuniversitair voor Kernwetenschappen), the NFWO (National Fonds voor Wetenschappelijk Onderzoek), the Geconcerteerde Acties, and the PREST Program (Ministrie van Wetenschapsbeleid) are gratefully acknowledged for financing this work, as is the IWONL (Instituut voor Wetenschappelijk Onderzoek in Nijverheid en Landbouw) for financial support to one of the authors (I.H.).

---


\textsuperscript{4}F. Rodríguez and M. Moreno, Solid State Commun. 58, 701 (1986).


\textsuperscript{8}S. Bencic, R. Cappeletti, F. Fermi, M. Manfredi, J. Z. Damm, and E. Mugenski, J. Lumin. 18/19, 341 (1979).


