Site-switched Tl⁰ atoms in Tl⁺-doped NaCl and KCl

I. Heynderickx, E. Goovaerts, S. V. Nistor,* and D. Schoemaker

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

The properties of two new Tl⁰-atom defects with orthorhombic symmetry ($[1\bar{1}0]$, [001], [110]) and which occur together with the well-known Tl⁰(1) center are studied in KCl:TlCl and NaCl:TlCl using electron-spin-resonance and optical-absorption techniques. On the basis of their production and their thermal and optical properties and taking into account the results of the hyperfine-interaction analysis it is concluded that these centers consist essentially of a Tl⁰ atom on an anion site (possibly perturbed by one or more cation vacancies), and that their production involves a site switching of the Tl⁰ atom in the Tl⁰(1) center. A Jahn-Teller distortion determines the symmetry of these defects and yields a ground-state p orbital oriented along a $\langle 110 \rangle$ direction. Similar site-switched models were proposed earlier for orthorhombic In⁰ and axial Ga⁰ centers in KCl, and it is shown that these centers possess many features in common with the orthorhombic Tl⁰ centers. One of the latter centers is optically very stable and forms the dominant defect in NaCl:TlCl while it is not produced in KCl. Optical-absorption bands at 430 and 560 nm are attributed to this center.

I. INTRODUCTION

During the last few years a number of centers have been extensively studied in weakly and heavily Tl⁺-doped alkali halides that have been exposed to ionizing radiation. One of those defects, namely the so-called Tl⁰(1) center, is laser active. From an ESR analysis in KCl,[1] RbCl,[2] KBr,[2] and NaCl,[3] it was determined that the Tl⁰(1) center consists of a Tl⁰ atom on a cation site, associated with an anion vacancy in a nearest-neighbor position along a $\langle 100 \rangle$ axis. Its luminescence properties near 1.5 μm have been reported in many alkali halides.[4,5] A mode-locked laser around 1.5 μm has been constructed using the Tl⁰(1) center in KCl and the 1.064-μm emission of a Nd:YAG laser (where YAG denotes yttrium-aluminum-garnet) was employed as a pump source.[4,6] Because the laser activity of the Tl⁰(1) may be interfered with by the presence of other Tl-related defects, a considerable effort has been spent recently to identify their structures and properties using a variety of experimental techniques.

In the heavily Tl-doped alkali halides several dimer and trimer centers, such as $Tl_2^+\langle 110 \rangle$,[7,8] $Tl_2^+\langle 111 \rangle$,[9] Tl⁺-perturbed Tl⁰(1),[10] and Tl_2^{3+},[11] occur together with the Tl⁰(1) center. For the Tl⁺-perturbed Tl⁰(1) center in KCl and RbCl it is known that one of its absorption bands overlaps with the near-infrared absorption band of the Tl⁰(1) center at 1.05 μm. In weakly doped KCl crystals, in which no dimer centers are produced, electron-spin-resonance (ESR) measurements[1] have revealed the existence of the Tl⁰(2) defect, consisting of a Tl⁰ atom on a cation site, flanked by two anion vacancies. Single-atom defects similar to the thallium-atom centers were recently discovered[12] by ESR in KCl crystals doped with the heavy metal ions Ga⁺ and In⁺. In Fig. 1 the defect structure of the primary electron trap $M^0(0)$ ($M=$Tl, In, or Ga),[12,13] and also the models of the $M^0(1)$ and $M^0(2)$ centers are depicted. Both in Ga⁺- and in In⁺-doped crystals one other type of center has been observed after x irradiation at room temperature (RT). In KCl:InCl the defect has

orthorhombic symmetry along, e.g., the ($[1\bar{1}0]$, [001], [110]) axes and is called the In⁰(ortho) center. In KCl:GaCl the so-called Ga⁰(axial) center seems to be the analogue of the In⁰(ortho) center, although its ESR spectrum is axial around a $\langle 100 \rangle$ axis. This axial symmetry of the ESR spectrum has been explained[12] by assuming the existence of a rapid reorientation motion around a $\langle 100 \rangle$ axis of an orthorhombic Ga⁰ defect whose structure is similar to In⁰(ortho).

In this paper we present data on several orthorhombic Tl⁰ centers in KCl and NaCl whose properties and structure closely resemble those of In⁰(ortho) and Ga⁰(axial). In Ref. 12 it was proposed that in the case of the latter two centers the In⁰ and Ga⁰ atoms occupied anion sites. The more extensive data to be given in the present paper for the orthorhombic Tl⁰ centers strongly point in the same direction. The process of site switching of a metal
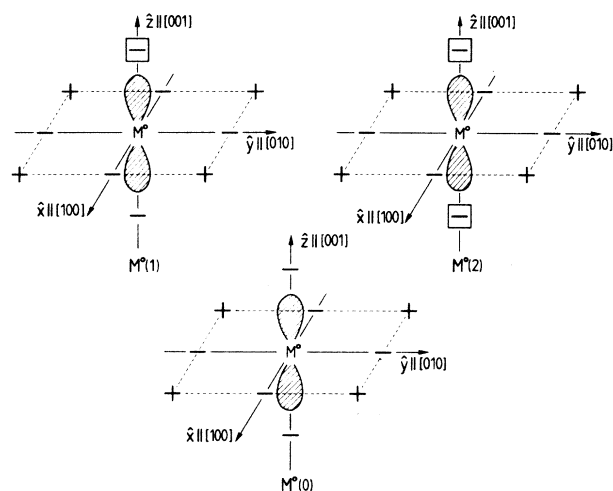

FIG. 1. $M^0(0)$, $M^0(1)$, and $M^0(2)$ defects ($M=$Ga, In, or Tl) in KCl consisting of a metal atom M^0 on a cation site without or with one or two disturbing anion vacancies in nearest-neighbor positions. The ground-state p-orbital of the M^0 atom is schematically indicated.

TABLE I. Spin-Hamiltonian parameters for the orthorhombic defects in Tl^+-doped NaCl and KCl crystals. The hf parameters correspond to the ^{205}Tl isotope, which has the largest natural abundance. The hf values and the reduced linewidth are given in mT.

Crystal	Defect	g_x [1Ī0]	g_y [001]	g_z [110]	A_x[a] [1Ī0]	A_y[a] [001]	A_z[a] [110]	ΔH_{red}[b]
NaCl	Tl^0(ortho,I)	1.263 ±0.002	1.200 ±0.002	1.799 ±0.003	−494.0 ±0.5	−491.8 ±0.5	+221.3 ±0.5	2.3 ±0.5
NaCl	Tl^0(ortho)	1.231 ±0.002	0.998 ±0.002	1.684 ±0.003	−521.9 ±0.5	−471.0 ±0.5	+231.8 ±0.5	2.6 ±0.5
KCl	Tl^0(ortho)	0.969 ±0.001	0.778 ±0.001	1.632 ±0.003	−550.0 ±2.0	−541.0 ±2.0	+293.0 ±2.0	2.2 ±0.5

[a]Signs are attributed to the hf parameters according to the analysis given in Sec. II C, which is based on Refs. 21 and 22.
[b]The reduced linewidth ΔH_{red} is determined from the experimental linewidth ΔH by $\Delta H_{red} = (g/g_0)\Delta H$.

atom or ion from a cation to an anion lattice site has been previously observed in Cu^{2+}-, Ag^+-, and Au^+-doped alkali halides in which substitutional Cu^- (Ref. 14), Ag^- (Refs. 14 and 15), and Au^- (Ref. 16) ions, respectively, are produced as a result of electrolytic or additive coloration. More recently we have presented ESR studies on Sn^- (Ref. 17) and Pb^- (Ref. 18) defects in x irradiated $KCl:SnCl_2$ and $KCl:PbCl_2$ crystals. However, in the case of the neutral Ga^0, In^0, and Tl^0 atoms in alkali halides there is nothing against them being located substitutionally in either a cation or an anion position. A similar situation was reported for the H^0 atom in alkali halides[19] substitutionally positioned either in a positive- or a negative-ion site, as was demonstrated by ESR and electron-nuclear double-resonance (ENDOR) experiments.

In Sec. II we present the results of the ESR analysis in NaCl of two new Tl^0 centers, one of which also occurs in KCl. The dominant orthorhombic defect, called Tl^0(ortho,I) is produced only in NaCl, both in weakly and heavily doped crystals. The other defect with much weaker ESR signals is only observed in weakly doped NaCl and KCl crystals and will be called the Tl^0(ortho) defect. As will be discussed in Sec. IV, the latter defect seems to be the analogue of the In^0(ortho) and Ga^0(axial) defects in KCl. The production properties of both Tl^0 defects are given in Sec. III, in which evidence is also presented for the optical and thermal transformation of $Tl^0(1)$ into Tl^0(ortho,I) defects in NaCl. The proposed defect structures and production mechanisms are discussed in Sec. IV.

The Tl^0(ortho,I) defect in NaCl is studied in a $NaCl:Tl^+$ crystal grown by the Bridgman-Stockbarger method from a melt of NaCl to which 2 mol % TlCl was added. The weakly doped KCl and NaCl crystals are grown by the Kyropoulos method, using a melt of KCl with 0.05 mol % TlCl and a melt of NaCl with 0.2 mol % TlCl. The experimental details and the treatment of the specimens are the same as described in Ref. 3.

II. ESR ANALYSIS OF THE ORTHORHOMBIC Tl^0 CENTERS IN NaCl AND KCl

A. The Tl^0(ortho,I) defect in NaCl

The ESR spectra of the so-called Tl^0(ortho,I) defect in NaCl, which is produced by a 90-min x irradiation at RT

and a subsequent annealing to 410 K, are shown in Fig. 2 for the external static magnetic field $\bar{H}$ oriented along $\langle 100 \rangle$ and $\langle 110 \rangle$. The resonance lines, measured at 15 K, can be seen over the whole temperature range from 8 to more than 100 K without a noticeable change in line position or in linewidth (given in Table I). The absence of a line broadening for increasing temperature indicates that no rapid motional effects occur in the temperature range up to 100 K. At the lowest temperature the Tl^0(ortho,I) defect saturates for power levels of about 1 mW, while 10 mW is needed to saturate the $Tl^0(1)$ center, the resonance lines of which are also indicated in Fig. 2.
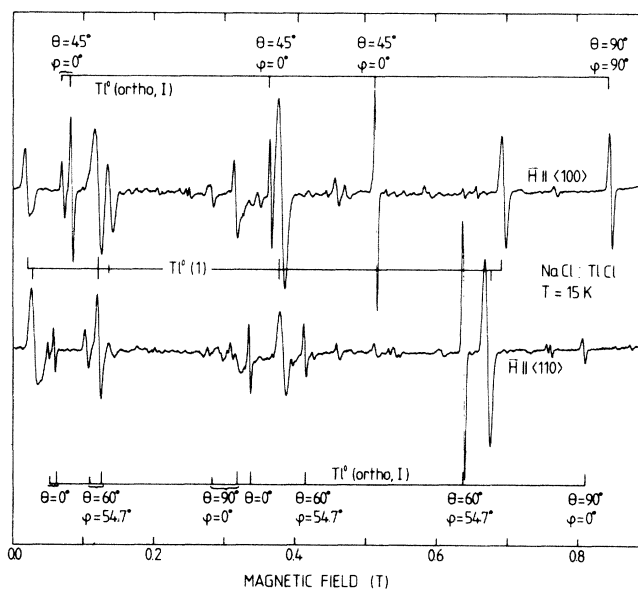

FIG. 2. ESR spectra (microwave frequency $\nu = 9.28$ GHz) measured at 15 K of a $NaCl:TlCl$ crystal, which was x-irradiated for 90 min at RT and subsequently annealed for 2 min at 410 K. The external static magnetic field is oriented along a $\langle 100 \rangle$ and a $\langle 110 \rangle$ crystallographic axis. The resonance lines of the Tl^0(ortho,I) defect are labeled by the polar angles (θ, ϕ) of the magnetic field with respect to the ([1Ī0], [001], [110]) axes. Isotope-split lines are connected by a curly brace.

The angular variation in a {100} plane shows that the Tl⁰(ortho,I) defect possesses orthorhombic symmetry with a set of axes (x,y,z) along, e.g., ([1̄10],[001],[110]). The resonance lines are labeled in Fig. 2 by the polar angles (θ,φ) which define the orientation of the external static magnetic field H with respect to the center axes (x,y,z). The g and hyperfine (hf) parameters were determined by a numerical analysis on the basis of the spin Hamiltonian (usual notation):

$$\frac{\mathscr{H}}{g_0\mu_B} = \overline{H}\cdot\overline{\overline{g}}\cdot\overline{S} + \overline{S}\cdot\overline{\overline{A}}\cdot\overline{I} \tag{1}$$

in which the electron spin $S=\frac{1}{2}$, and the nuclear spin $I=\frac{1}{2}$ for both Tl isotopes. The ESR parameters are given in Table I. The experimental angular dependence of the line positions and intensities was faithfully reproduced by substituting these parameters into Hamiltonian (1). This calculation also reveals the existence of three forbidden transitions, one for the magnetic field along each of the center axes. These transitions become progressively allowed when H turns away from these axes. The absence of the clearly separated high- and low-field hf lines, which are characteristic for ESR spectra of an $S=\frac{1}{2}$ system interacting with a single $I=\frac{1}{2}$ nucleus, as well as the existence of forbidden transitions, are caused by the zero-field splittings, which are larger than the microwave energy $h\nu$ ($\nu\simeq9.3$ GHz, h is Planck's constant) as a result of the strong hf interaction.

The occurrence of two Tl isotopes, ²⁰³Tl and ²⁰⁵Tl with natural abundances of 30% and 70%, respectively, both with nuclear spin $I=\frac{1}{2}$, but with slightly different nuclear moments (²⁰³$\mu_I=1.6115$ and ²⁰⁵$\mu_I=1.6274$ nuclear magnetons), is responsible for the observed splitting in several low-field resonance lines (see Fig. 2). For the other lines of the Tl⁰(ortho,I) defect in NaCl a calculation of the line positions with hf parameters scaled according to the ratio of the nuclear moments confirmed that the isotopic splitting is smaller than the linewidth.

B. The Tl⁰(ortho) centers in NaCl and KCl

The resonance lines of the Tl⁰(ortho) defects in NaCl and KCl are rather weak and can only be resolved from the Tl⁰(1) resonance lines in weakly doped NaCl or KCl crystals, which are bleached at RT in the "F-like" Tl⁰(1) absorption band [$\lambda=470$ nm in NaCl (Ref. 3) and 550 nm in KCl (Ref. 20)] after 1 h of x irradiation at RT.

In KCl the Tl⁰(ortho) defect saturates at higher microwave powers and lower temperatures than the Tl⁰(1) center. This behavior is the opposite in the NaCl crystals: the Tl⁰(ortho) defect in NaCl saturates faster than the Tl⁰(1) center, but still slower than the Tl⁰(ortho,I) center. No changes in the line position or the linewidth (given in Table I) were observed for increasing temperatures. An angular variation in a {100} plane is shown in Fig. 3 for KCl and demonstrates the orthorhombic symmetry of the Tl⁰(ortho) defect with the same local axes as for Tl⁰(ortho,I), e.g., ([1̄10],[001],[110]).

The g and hf parameters, given in Table I for the Tl⁰(ortho) defect in KCl and NaCl, are calculated for the ²⁰⁵Tl isotope on the basis of the spin Hamiltonian (1).
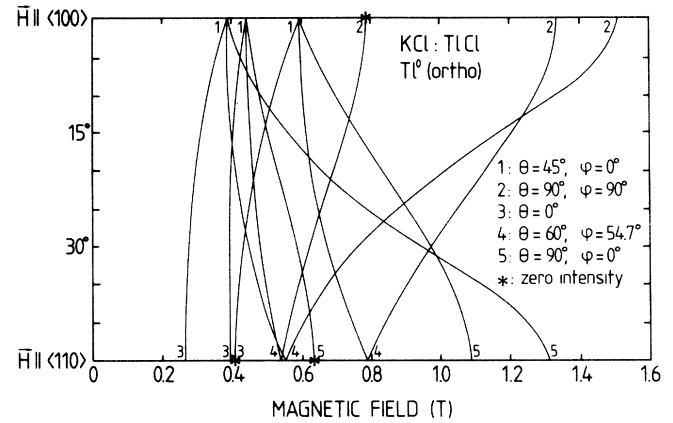

FIG. 3. Angular dependence of ESR resonances of Tl⁰(ortho) in KCl calculated with the ESR parameters given in Table I for a microwave frequency $\nu=9.28$ GHz. The transitions marked with an asterisk are forbidden.

One of the three ESR transitions becomes forbidden when the magnetic field approaches a principal direction x, y, or z of the defect, as is indicated in Fig. 3 by an asterisk. This results from the large hf interaction and occurs for the same pairs of energy levels in KCl and NaCl. A calculation of the angular variation, but with the hf parameters scaled according to the ratio of the nuclear moments of both Tl isotopes, yields an isotopic splitting observable only for the lowest set of resonance lines. This agrees with the experimental observations for Tl⁰(ortho) in both hosts.

C. Discussion of the thallium hyperfine interaction

From the hf parameters, given in Table I for the orthorhombic Tl⁰ defects in both hosts, one can calculate the isotropic, A_σ, and the anisotropic, p, contribution of the hf interaction using formula (3) of Ref. 21. This formula was derived on the basis of a simple crystal-field model for np^1 heavy metal ions or atoms under the influence of a tetragonal crystal field. The calculation of the p and A_σ value from the Tl⁰(ortho) defect parameters in KCl and NaCl uses this approximation of axial symmetry for the g tensor in spite of the quite large anisotropy in the perpendicular g components for these defects (see Table I). The p and A_σ values are compared in Table II to the corresponding values of Tl⁰(1) in NaCl and KCl.[22]

From this comparison we find that the p value is almost constant throughout the series of Tl⁰ defects as expected for the atomic parameter which is determined by the $\langle r^{-3}\rangle$ value of the $6p$ orbital and which describes the dipole-dipole interaction of the electron spin with the nuclear spin. The A_σ value is strongly dependent on the specific defect and reflects the influence of the crystal field on the isotropic hf interaction. The sign of this quantity is mainly determined by the relative size of a negative contribution A_σ^e, caused by the exchange polarization of the inner s orbitals, and a positive contribution A_σ^s, introduced by s mixing into the ground orbital of the np^1 ion.[21] This s mixing is only parity allowed when the

TABLE II. Anisotropic part ρ, and isotropic part A_σ, of the hf interaction for the orthorhombic defects in NaCl and KCl, doped with Ga^+, In^+, and Tl^+, compared to the values of the corresponding $M^0(1)$ defects $(M=$ Ga,In,Tl$)$. All values are given in mT.

Crystal	Defect	ρ	A_σ	Defect	ρ	A_σ
NaCl	Tl^0(ortho,I)	113	-164			
NaCl	Tl^0(ortho)	113	-192	$Tl^0(1)$[a]	105	$+254$
KCl	Tl^0(ortho)	109	-159	$Tl^0(1)$[a]	97	$+76$
KCl	In^0(ortho)[b]	10.3	-18.6	$In^0(1)$[b]	12.6	$+10.8$
KCl	Ga^0(axial)[b]	7.9	-13.3	$Ga^0(1)$[b]	8.9	$+5.0$

[a]Reference 22.
[b]References 12 and 21.

crystal field acting on the ground orbital of the ion contains a sufficiently large odd component. Using the results obtained in Refs. 21 and 22 we can confidently conclude from the negative A_σ values of the orthorhombic defects that they are exposed to an essentially even crystal field, whereas, e.g., in the $Tl^0(1)$ defects an odd crystal-field component gives a relatively large positive contribution to the hf interaction. However, a negative A_σ value does not necessarily imply that the defect structure of the orthorhombic defects possesses exact inversion symmetry. Reflection symmetry with respect to the plane perpendicular to the p_z ground orbital of the np^1 ion will also prohibit s mixing, and thus only the sizable negative A_σ value, characteristic of the free np^1 atom, remains.

III. PRODUCTION OF THE ORTHORHOMBIC Tl^0 DEFECTS FROM THE $Tl^0(1)$ CENTER

A. Production, optical, and stability properties of the Tl^0 centers in NaCl and KCl

The small concentration of the Tl^0(ortho,I) defect, which is observed in NaCl immediately after a long x irradiation of about 90 min at RT or at higher temperatures up to 350 K, can be increased considerably in several ways. This will be discussed in the next paragraph. It follows from our experiments that the Tl^0(ortho,I) defect is never produced in total absence of $Tl^0(1)$ centers. This implies that a direct production below 260 K is impossible, since in NaCl the anion vacancies necessary to produce the $Tl^0(1)$ centers are not mobile at those temperatures.[3]

The most efficient way to produce a strong Tl^0(ortho,I) concentration is an x irradiation at RT, followed by a short (±2 min) annealing to 420 K. The pulse-anneal experiment above RT, given in Fig. 4 for a NaCl:TlCl crystal which was x-irradiated at RT for 90 min, illustrates that the amount of Tl^0(ortho,I) reaches a maximum at the temperature where the $Tl^0(1)$ concentration is strongly decreasing. However, both centers disappear at about the same temperature, around 480 K. The Tl^0(ortho,I) concentration can also be increased after x irradiation at RT by keeping it at this temperature for several days. After a week the amount of Tl^0(ortho,I) increased by 30% and a subsequent pulse-anneal experiment similar to the one mentioned above gives another 20% increase for an an-

nealing temperature of 420 K. Finally, the Tl^0(ortho,I) concentration can be increased more than 3 times by an F bleach ($\lambda=455$ nm) at RT of a crystal x-irradiated also at RT. Long illumination times (of the order of 1 h) were necessary to saturate this intensity increase, while the intensity of the $Tl^0(1)$ defect reaches a maximum after ±5 min of illumination.

The production properties of the Tl^0(ortho) defect in KCl and NaCl are quite similar to those of Tl^0(ortho,I) in NaCl, except for the lower optical and thermal stability. The very small amount reached after long x irradiations at RT, can be somewhat increased by a pulse anneal to higher temperatures, reaching a maximum intensity at 375 K in NaCl and at 350 K in KCl. An even stronger Tl^0(ortho) concentration by a factor 4 can be obtained after an x irradiation at RT followed by bleaching at this temperature the F-like $Tl^0(1)$ absorption band ($\lambda=550$ nm in KCl and 470 nm in NaCl). Saturation of this intensity increase is reached after 25 min of bleaching in KCl and 60 min in NaCl. This saturation for the Tl^0(ortho) defect in NaCl is about a factor 2 faster than the saturation of the Tl^0(ortho,I) defect measured during the same bleaching experiment. The maximum concentration obtained in this way for the Tl^0(ortho) defect in
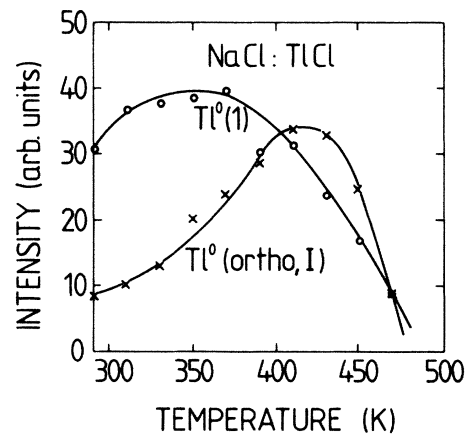

FIG. 4. Pulse-anneal experiment of a NaCl:TlCl crystal after 90 min of x irradiation at RT. The intensity of the Tl^0(ortho,I) defect is compared to the intensity of the $Tl^0(1)$ center, both measured at 15 K after 2 min of annealing at each temperature.

NaCl is estimated to be about 10 times smaller than the maximum concentration of the Tl^0(ortho,I) defect and it is impossible, even in the weakly Tl^+-doped crystals, to produce Tl^0(ortho) in the same amounts as Tl^0(ortho,I). The thermal stability of the Tl^0(ortho) center is lower than the thermal stability of the Tl^0(1) center. The Tl^0(ortho) defect disappears around 410 K in both hosts, a temperature about 70 K below the decay temperature of the Tl^0(1) center.

B. The relation between the Tl^0(1) and Tl^0(ortho,I) defect in NaCl

From the production properties of the Tl^0(ortho,I) defect we conclude that its intensity increases considerably when the Tl^0(1) center decays. This suggests that the Tl^0(1) center is converted into Tl^0(ortho,I) by thermal or optical excitation. This is further supported by the following optical experiments on those two Tl^0 defects in NaCl.

In Fig. 5 the results are shown of bleaching at RT in the 470-nm Tl^0(1) absorption band in a NaCl:TlCl sample, which was previously x-irradiated at RT for 2 h. The initial increase in the Tl^0(1) concentration is caused by the optical bleaching of the F centers, the absorption band ($\lambda = 455$ nm) of which overlaps the Tl^0(1) absorption band. After 5 min of bleaching, the Tl^0(1) concentration starts to decrease while Tl^0(ortho,I) still increases. The two intensity changes saturate after about 90 min of bleaching, when nearly all of the Tl^0(1) centers have been destroyed.

When the same experiment is repeated, but with a bleaching temperature of 220 K, we observe not only a reorientation of the Tl^0(1) centers towards the $\langle 100 \rangle$ direction parallel to the propagation of the light beam, i.e., the direction perpendicular to the possible orientation of the random polarization, but also a decrease of the total Tl^0(1) concentration. This decrease is, however, smaller than for a bleaching at RT. During a subsequent anneal 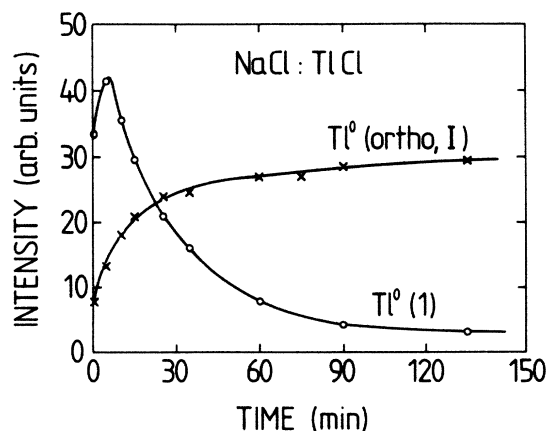to RT the Tl^0(1) centers are redistributed over all the $\langle 100 \rangle$ directions. Moreover, after this anneal part of the bleached Tl^0(1) centers are restored, and also an increase in the concentration of the Tl^0(ortho,I) centers is observed. This points to a conversion from Tl^0(1) to Tl^0(ortho,I). Part of this conversion occurs during the anneal to RT, but part of it has already taken place during the bleach at 220 K. This means that the mobility of the anion vacancy is not involved in the production of Tl^0(ortho,I) from Tl^0(1). On the other hand, cation vacancies are mobile in NaCl around 220 K,[22,23] and consequently they may be involved in the conversion process.

The possibility of transforming Tl^0(ortho,I) centers back into Tl^0(1) centers was examined by bleaching of a NaCl crystal, in which almost all Tl^0(1) had been converted into Tl^0(ortho,I), in an absorption band of the Tl^0(ortho,I) defect. Indeed, by correlating the ESR production and stability properties of the Tl^0(ortho,I) defect with optical-absorption data we have identified two absorption bands of the Tl^0(ortho,I) center, one at 430 nm and a much weaker band at 560 nm. Figure 6 presents absorption spectra of a NaCl:TlCl crystal, x-irradiated for 2 h at RT. Spectrum a is recorded after 5 min of excitation at RT with 455-nm light, which results in bleaching of the F centers and an optimal production of Tl^0(1), which possesses a strong absorption band at 470 nm.[3] A continued bleach at this wavelength results in the decay of Tl^0(1) and the appearance of the bands attributed to Tl^0(ortho,I) (see Fig. 6, spectrum b) The identification is further confirmed by an optical excitation experiment at RT with 430-nm light polarized along $\langle 110 \rangle$. The Tl^0(ortho,I) centers with the z axis along the polarization vector were reoriented preferentially as observed in ESR

FIG. 5. ESR intensities measured at 15 K of the Tl^0(1) and Tl^0(ortho,I) centers in a NaCl:TlCl crystal, x-irradiated for 90 min at RT, are given as a function of the bleaching time at RT in the absorption band of the Tl^0(1) center at 470 nm.
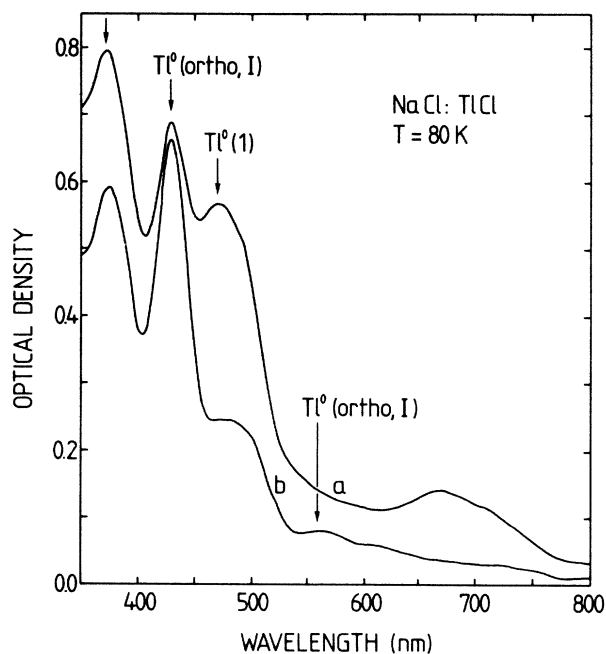

FIG. 6. Optical-absorption spectrum at 80 K of a NaCl:TlCl crystal, x-irradiated for 2 h at RT and subsequently F-bleached ($\lambda = 455$ nm) at the same temperature: a, after 5 min of F bleaching; and b, after 55 min of F bleaching.

from the decrease of the $\theta = 0°$ line intensity measured with the magnetic field H parallel to the optical polarization. This experiment gives the additional information that the 430-nm absorption band of the $Tl^0(ortho,I)$ defect in NaCl is predominantly σ-polarized.

However, bleaching at RT in the 430-nm absorption band causes an increase in the $Tl^0(1)$ concentration without a reduction in the $Tl^0(ortho,I)$ concentration. This result can only be explained by accepting the existence of another Tl defect, which absorbs 430-nm light to produce $Tl^0(1)$ centers. As soon as all these other Tl centers are bleached, the $Tl^0(1)$ concentration starts decreasing again, as is observed for a long excitation at 430 nm at RT. Even during this long bleach the $Tl^0(ortho,I)$ concentration does not decrease.

Finally, we can remark that the strong absorption band at 370 nm, present in Fig. 6, is not related to the $Tl^0(1)$ or the $Tl^0(ortho,I)$ centers. This is proved by the lack of correlation for the production and stability properties between the ESR and the optical-absorption results. Moreover, a preferential bleaching experiment at RT in this band caused neither reorientation nor bleaching effects of those defects. Also, this absorption band, which partially overlaps with the 430-nm band, is not responsible for the increase in the $Tl^0(1)$ concentration, observed for a 430-nm bleach at RT.

IV. DISCUSSION

A. Comparison of $Tl^0(ortho)$ with $In^0(ortho)$ and $Ga^0(axial)$

In Table III the g parameters of the $Tl^0(ortho)$ defect in NaCl and KCl are compared with the same parameters of the $In^0(ortho)$ and $Ga^0(axial)$ centers in KCl.[12] The $In^0(ortho)$ center possesses the same symmetry as described in Sec. II for the orthorhombic Tl^0 defects. Since for the $Ga^0(axial)$ defect an averaging motion in a $\{100\}$ plane is proposed as the origin for the axial symmetry of the ESR spectrum, one can calculate[12] the g parameters for the static orthorhombic defect in an axial approximation and these are given in Table III. From the comparison of the g parameters we see that the $M^0(ortho)$ defects $(M = In, Tl)$ and the $Ga^0(axial)$ defect are characterized by a weaker crystal field than the corresponding $M^0(1)$ defects $(M = Ga, In, Tl)$ as is evidenced by the higher g shifts. Moreover, the $M^0(ortho)$ defects exhibit

quite a large difference between their g_x and g_y components, pointing to a strong orthorhombic distortion. For $Tl^0(ortho,I)$ the g values (given in Table I) are very comparable to those of $Tl^0(1)$ and the departure from axial symmetry is quite small.

The ρ and A_σ values, calculated from the hf parameters of Table I, are compared in Table II for all these defects. This demonstrates, as was pointed out in Ref. 20, that in all of these centers the np^1 atom is influenced by an essentially even crystal field.

The production at higher temperatures, and the lower thermal stability of the $In^0(ortho)$ and the $Ga^0(axial)$ defect compared to the corresponding $M^0(1)$ defect $(M = Ga, In)$, as described in Sec. V of Ref. 12, are analogous to the same properties of the $Tl^0(ortho)$ defect in NaCl and KCl, described in Sec. III A.

All these results lead to the conclusion that the $Tl^0(ortho)$ defect in KCl and NaCl possesses a structure similar to that of the $In^0(ortho)$ and $Ga^0(axial)$ defect in KCl. On the contrary, the $Tl^0(ortho,I)$ defect in NaCl is found to be a specific and dominant defect for which no analogous structure in KCl crystals doped with np^1 impurity atoms is found.

B. Models for the orthorhombic defects based on site-switching processes

The similarities between the orthorhombic Tl^0 and In^0 centers and the $Ga^0(axial)$ defect, which are discussed in the preceding section, lead us to propose models with the same basic characteristics for all of these centers. Already several defects have been studied in these crystals consisting of a metal atom M^0 $(M = Ga, In, or Tl)$ on a positive-ion site with either one or two neighboring anion vacancies, namely the $M^0(1)$ and $M^0(2)$ centers, respectively. In order to obtain defects with orthorhombic symmetry one can assume the presence of even more anion and/or cation vacancies (see Ref. 12). Some of these "vacancies" models must be eliminated because of their high effective charge. Furthermore, one has to take into account the constraint derived from the hf analysis (Sec. II C) that the crystal field acting on the np^1 atom must be either dominantly even or possess a reflection plane perpendicular to the $\langle 110 \rangle$-oriented z axis. Finally, it would be very difficult in such vacancies models for the orthorhombic centers to envisage a fast averaging motion around a

TABLE III. g parameters of the $Tl^0(ortho)$ defect in KCl and NaCl and of the $In^0(ortho)$ and $Ga^0(axial)$ defects in KCl are compared to the g values of the corresponding $M^0(1)$ defects $(M = Ga, In, Tl)$. The precision of the g parameters is ± 0.003.

Crystal	Defect	g_x [$1\bar{1}0$]	g_y [001]	g_z [110]	Defect	$g_\perp$	$g_{\parallel}$
NaCl	$Tl^0(ortho)$	1.231	0.998	1.684	$Tl^0(1)$[a]	1.266	1.732
KCl	$Tl^0(ortho)$	0.969	0.778	1.632	$Tl^0(1)$[a]	1.308	1.789
KCl	$In^0(ortho)$[b]	1.695	1.806	1.967	$In^0(1)$[b]	1.848	1.984
KCl	$Ga^0(axial)$[c]		1.894	2.000	$Ga^0(1)$[b]	1.953	1.998

[a]Reference 22.
[b]Reference 12.
[c]The parameters given for the $Ga^0(axial)$ defect are the calculated parameters for the static defect in axial approximation (Ref. 12).

⟨100⟩ axis such as was proposed for the Ga⁰(axial) defect.[12]

Switching the metal atom from its initial cation to an anion site was already put forward as a possibility for Ga⁰(axial) and In⁰(ortho) in KCl.[12] It leads to a series of simple models which permit one to a large extent to understand the properties of the centers of interest here. In each of these models (see Fig. 7) the defect structure is dominated by an orthorhombic Jahn-Teller distortion of the surroundings. The p_z orbital with the lowest energy is schematically drawn in the figure and determines the near to axial symmetry of the defect around $z||⟨110⟩$. Each of the models possesses reflection symmetry perpendicular to this axis as required by the analysis of the hf data (Sec. II C).

In Sec. III B we have presented experimental evidence for the optically or thermally activated transformation of Tl⁰(1) into Tl⁰(ortho,I) in NaCl. A simple site switching of the Tl⁰ atom in the Tl⁰(1) center would lead to the first of our models [Fig. 7(a)]. Apart from the question as to whether it is likely to have two stable defect configurations for a Tl⁰ atom in a single divacancy, this model is not an acceptable one for the Tl⁰(ortho,I) center for the following reasons. Optical excitation in the 470-nm band below 200 K does not produce Tl⁰(ortho,I). This is not readily understood if only the switching of sites is necessary for the transformation. Moreover, it was shown that a small increase of Tl⁰(ortho,I) concentration results from a similar optical excitation around 220 K, i.e., well below the temperature for mobility of anion vacancies. In this temperature region, however, the cation vacancies become mobile as is known from a study of several Fe⁺ and Sn⁺ centers in Fe²⁺- or Sn²⁺-doped NaCl.[23,24] It is therefore reasonable to assume that either an additional cation vacancy is trapped at the Tl⁰ atom or, on the contrary, that the cation vacancy of the first model [Fig. 7(a)] moves away from this atom. This would lead to the models of Figs. 7(b) and 7(c), respectively.

Each of the latter two defect structures has its own drawbacks as a model for the Tl⁰(ortho,I) center. For the vacancy trapping a relatively large amount of mobile cation vacancies must be available which can only be pro-

FIG. 7. Three models for the orthorhombic defects in KCl:InCl, KCl:TlCl, and NaCl:TlCl and for Ga⁰(axial) in KCl, in which the heavy metal atom M^0 is situated on an anion site.

vided by divalent ions present as accidental impurities in the samples (such as, e.g., Fe²⁺). Moreover, it is hard to understand how this could lead to a thermally very stable defect such as Tl⁰(ortho,I). On the other hand, moving the cation vacancy away from Tl⁰ on an anion site is counteracted by the Coulomb attraction between these charged entities. It is possible, however, that an intermediate step is involved such as the trapping of an electron prior to or after the site switching. This will eliminate the Coulomb attraction with the vacancy which can then move away. A subsequent optical or thermal ionization of the resulting Tl⁻ would lead to the defect shown in Fig. 7(c). The increase of Tl⁰(ortho,I) intensity during warmup to RT consecutive to the Tl⁰(1) bleaching at 220 K (Sec. III B) is an indication for such a two-step production process. One would expect such a center to be very stable against thermal decay and against optical excitation in its 430-nm absorption band, as is experimentally observed. Also in favor of this model is the fact that compared to the Tl⁰(ortho) center the Tl⁰(ortho,I) center possesses only a small orthorhombic component in the g and hf tensors.

The Tl⁰(ortho,I) center is not at all observed after x irradiation of NaCl:TlCl at 77 K and subsequent warmup to RT. At this stage optical excitation of Tl⁰(1) in the 470-nm band does not result in production of Tl⁰(ortho,I). This observation is hard to reconcile with any of the proposed production sequences. Finally, it is not well understood why this center, which is very efficiently produced in NaCl, does not appear in KCl.

Unfortunately, less information is available about the production of Tl⁰(ortho), In⁰(ortho), and Ga⁰(axial) starting from the corresponding $M^0(1)$ defects. We notice the fact that the $M^0(1)$ center is always produced together with, or before, the appearance of the "site-switched" centers, and we will assume that the first steps in their production sequence are essentially the same as in the case of Tl⁰(ortho,I). Their lower thermal stability points to the model involving two cation vacancies [Fig. 7(b)] in which one vacancy is not bound by Coulomb forces and can easily move away from the neutral entity which is left. The concentration then essentially depends on the amount of mobile cation vacancies in the crystal, and less on the intentional Ga⁺, In⁺, or Tl⁺ doping level. This would explain why in KCl:TlCl and NaCl:TlCl with smaller Tl⁺ concentration the Tl⁰(ortho) possesses a higher ESR intensity relative to that of Tl⁰(1). Confirmation of the models proposed in this paper for the orthorhombic Tl⁰ centers awaits the application of more direct experimental techniques such as ENDOR.

In Ref. 12 it was proposed that the Ga⁰(axial) center in fact possesses orthorhombic symmetry, but that a fast motion takes place which yields an average axial ESR spectrum. In the models of Fig. 7 this would amount to a jump of the p_z orbital and the accompanying Jahn-Teller distortion from one ⟨110⟩ direction to another. In order to obtain ⟨100⟩ axial symmetry of the ESR spectra these jumps must be restrained to one {100} plane, which is achieved in models a and b by the presence of the cation vacancies. The model without vacancies is not suitable for this defect. The averaging motion is sufficiently fast
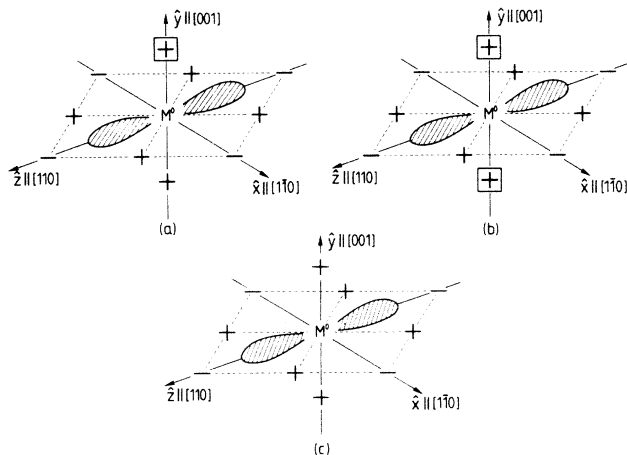
to yield the same ESR spectrum down to the lowest temperatures ($T\simeq 8$ K) which indicates a fast tunneling type of motion. Therefore, it is necessary that the energy barrier between the two possible orientations is lower than or comparable to vibrational energies, i.e., a dynamical Jahn-Teller effect occurs in the Ga^0(axial) defect in KCl.

Note added in proof. Our attention has been drawn to a report on Ag^0 atom centers in KCl:AgCl crystals with properties similar to our orthorhombic Tl^0 defects. Optical bleaching of a Ag^0 on a cation site and associated with an anion vacancy transforms it into an Ag^- center on an anion site (the well-known B center). The latter can in turn be bleached optically and transformed into an Ag^0 center on an anion site [N. I. Melnikov, P. G. Baranov, and R. A. Zhitnikov, Phys. Status Solidi B **46**, K73 (1971)].

*Permanent address: Central Institute of Physics, C.P. MG-7, R-76900 Magurele-Bucuresti, Romania.

[1]E. Goovaerts, J. Andriessen, S. V. Nistor, and D. Schoemaker, Phys. Rev. B **24**, 29 (1981).

[2]S. V. Nistor, E. Goovaerts, A. Bouwen, and D. Schoemaker, Phys. Rev. B **27**, 5797 (1983).

[3]S. V. Nistor, I. Heynderickx, E. Goovaerts, A. Bouwen, and D. Schoemaker, Phys. Status Solidi B **130**, 175 (1985).

[4]W. Gellermann, F. Luty, and C. R. Pollock, Opt. Commun. **39**, 391 (1981).

[5]M. Fockele, F. J. Ahlers, F. Lohse, J.-M. Spaeth, and R. H. Bartram, J. Phys. C **18**, 1963 (1985).

[6]L. F. Mollenauer, N. D. Vieira, and L. Szeto, Opt. Lett. **7**, 414 (1982).

[7]B.-r. Yang, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **27**, 1507 (1983).

[8]S. V. Nistor, D. Schoemaker, I. Ursu, and B.-r. Yang, Phys. Status Solidi B **127**, 657 (1985).

[9]S. V. Nistor, E. Goovaerts, B.-r. Yang, and D. Schoemaker, Phys. Rev. B **28**, 1219 (1983).

[10]F. J. Ahlers, F. Lohse, and J.-M. Spaeth, J. Phys. C **18**, 3881 (1985).

[11]Y. Toyotomi and R. Onaka, J. Phys. Soc. Jpn. **46**, 1861 (1979); **46**, 1869 (1979).

[12]W. Van Puymbroeck, J. Andriessen, and D. Schoemaker, Phys. Rev. B **24**, 2412 (1981).

[13]C. J. Delbecq, A. K. Gosh, and P. H. Yuster, Phys. Rev. **151**,

599 (1966); **154**, 797 (1967); P. G. Baranov and V. A. Khramtsov, Phys. Status Solidi B **101**, 153 (1980).

[14]W. Kleeman, Z. Phys. **249**, 145 (1971).

[15]W. Kleeman, Z. Phys. **214**, 285 (1968); F. Fisher, *ibid.* **231**, 393 (1970); K. Kojima, S. Shimanuka, and T. Kojima, J. Phys. Soc. Jpn. **33**, 1076 (1972).

[16]K. Kojima, M. Maki, and T. Kojima, J. Phys. Soc. Jpn. **28**, 1227 (1970); D. Lemoyne, J. Duran, M. Billardou, and Le Si Dang, Phys. Rev. B **14**, 747 (1976).

[17]F. Van Steen and D. Schoemaker, Phys. Rev. B **19**, 55 (1979).

[18]E. Goovaerts, S. V. Nistor, and D. Schoemaker, Phys. Rev. B **25**, 83 (1982).

[19]J.-M. Spaeth, in *Defects in Insulating Crystals, Riga, 1981*, proceedings of the International Conference, edited by V. M. Tuchkevich and K. K. Shvarts (Zinatne, Riga, and Springer, Berlin, 1981), p. 232.

[20]L. F. Mollenauer, N. D. Vieira, and L. Szeto, Phys. Rev. B **27**, 5332 (1983).

[21]D. Schoemaker, I. Heynderickx, and E. Goovaerts, Phys. Rev. B **31**, 5687 (1985).

[22]I. Heynderickx, E. Goovaerts, and D. Schoemaker, Solid State Commun. **55**, 877 (1985).

[23]B.-r. Yang, A. Bouwen, and D. Schoemaker, Phys. Status Solidi B **127**, 657 (1985); S. V. Nistor, M. Velter-Stefeinescu, and C. D. Matescu, Solid State Commun. **53**, 989 (1985).

[24]C. J. Delbecq, R. Hartford, D. Schoemaker, and P. H. Yuster, Phys. Rev. B **13**, 3631 (1976).