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Electron-spin-resonance study of Tl° centers of the laser-active type structure in $SrCl_2$

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The electron-spin-resonance spectra and production properties of two ⟨111⟩-oriented Tl^0 centers, called $Tl_c^0(1)$ and $Tl_i^0(1)$, have been carefully analyzed in x-ray-irradiated $SrCl_2$:TlCl crystals. It is shown that these two centers possess essentially the laser-active $Tl^0(1)$-type structure observed in the alkali-metal halides: The structural core is in both cases a Tl^0 atom perturbed by a nearest-neighbor anion vacancy. In the $Tl_c^0(1)$ center, directly produced by x-ray irradiation at liquid-nitrogen temperature, the Tl^0 occupies the cation site, whereas in $Tl_i^0(1)$ the Tl^0 occupies the empty interstitial site of the fluorite lattice and is associated with a divacancy in a linear configuration along ⟨111⟩. Apart from the study of the production properties, the analysis of the isotropic part of the hyperfine interaction has proved to be very valuable in identifying the microscopic defect structures and to differentiate between the models for the two defects. Our measurements establish that at least part of the substitutional Tl^+ dopant is charge compensated by an adjoining anion vacancy along ⟨111⟩. It is also found that in $SrCl_2$ the anion vacancy becomes mobile above 140 K, and the thermal conversion of $Tl_c^0(1)$ to $Tl_i^0(1)$, which involves site switching from the cation site to the empty interstitial site, may be helped by the incipient mobility of the anion vacancy.

I. INTRODUCTION

The $Tl^+(6s^2)$ ions incorporated in alkali-metal halide crystals act both as electron and hole trapping centers in crystals subjected to ionizing radiation, resulting in Tl^0 and Tl^{2+} species,[1-4] respectively. One of these trapped electron centers, the so-called $Tl^0(1)$ center,[3] has been shown to be laser active in the near-infrared region (≈1.5 μm) with stable and attractive laser properties in KCl.[5,6] From a thorough analysis of the electron-spin-resonance (ESR) data,[3] the hyperfine (hf) data in particular, it was found that in this center the Tl^0 atom experiences a strong odd crystal field and it was deduced that the $Tl^0(1)$ center consists of a Tl^0 atom on a cation site perturbed by one anion vacancy in the nearest-neighbor (NN) position along a ⟨100⟩ direction, hence the 1 between brackets. The odd crystal field, which makes transitions allowed between the spin-orbit and crystal-field-split levels of the ground np^1 manifold, lies at the heart of the optical excitation and luminescence properties, necessary (but not sufficient) for the laser-active properties of these centers.[7] As a result np^1 heavy-metal centers possessing an analogous structure are called *centers of the laser-active structure*, even though their laser activity may turn out to be poor or otherwise flawed.[8,9] The atom-in-odd-crystal-field model describes quite well the $Tl^0(1)$ states arising from the ground np^1 manifold. In the excited state associated with the atomic $7s^1$ configuration the electron orbital seems to be more *F* center like, i.e., the electron is mostly localized in the adjoining anion vacancy[10].

The ESR measurements also revealed the existence of several related Tl centers. The $Tl^0(2)$ defect[3] consists of a Tl^0 on a cation site flanked by two NN anion vacancies along ⟨100⟩, and thus experiences an even crystal field. In the site-switched Tl^0 centers[11] the Tl^0 is on an anion site and is possibly, but then only weakly, perturbed by a cation vacancy. In the site-switched center the Tl^0 undergoes a Jahn-Teller distortion leaving the unpaired electron in a *p* orbital oriented along ⟨110⟩. All the foregoing centers were produced either by direct irradiation at, or by subsequent warmup to, a temperature (T>220 K) where anion vacancies, also produced by the ionizing radiation, become mobile. These experiments have been extended to a large number of np^1 ($n = 4,5,6$) heavy-metal defects in various alkali-metal halides.[12]

In view of their laser activity there is a continued interest in searching for similar centers in crystals other than the alkali-metal halides, and ionic crystals with the perovskite and fluorite structures have received increasing attention. In this paper we report on centers of the laser-active structure in the alkaline earth $SrCl_2$ crystal. The alkaline earth halide crystals possess the fluorite structure, which may be thought of as a simple cubic lattice of halogen ions in which along the three ⟨100⟩ directions every other body center of an halogen cage is occupied by a divalent alkaline earth cation.

We have investigated the electron and hole trapping properties of the $6s^2$ heavy-metal ion impurities Tl^+ and Pb^{2+} in alkaline earth $SrCl_2$ crystals, and the results of the thallium doped crystal will be presented here. (Pb^+ defects have already been studied in three alkaline earth fluorides[13] and in the perovskite crystal[14] $KMgF_3$ doped with Pb^{2+}.) We will discuss the production and properties of two types of Tl^0 centers, called $\mathrm{Tl}_c^0(1)$ and $\mathrm{Tl}_i^0(1)$, observed in $\mathrm{SrCl_2{:}TlCl}$ crystals.

These centers both will be shown to possess structures similar to the laser-active $\mathrm{Tl}^0(1)$ structure in the alkali halides. The monovalent Tl^+ ion is found to enter the crystal in substitutional sites of the divalent host cations. It also follows from our experiments that, because of the specific way charge compensation occurs in the $\mathrm{SrCl_2}$ lattice, the precursor of the $\mathrm{Tl}_c^0(1)$ center is already present in the as-grown crystals as a substitutional Tl^+ ion associated with a charge compensating anion vacancy. As a result, a dominant fraction of the $\mathrm{Tl}_c^0(1)$ centers is produced directly by electron trapping at such precursor sites. It will further be shown that by a warmup to 140 K and above, the Tl^0 atom of the $\mathrm{Tl}_c^0(1)$ center can switch to the energetically favorable empty interstitial position of the fluorite lattice. The $\mathrm{Tl}_i^0(1)$ center is formed in this process and is thermally stable above room temperature (RT).

II. EXPERIMENT

Samples used in these experiments were cleaved from single crystals grown by the Bridgman technique in a reactive atmosphere inside closed quartz ampoules.[15] The starting material was extra pure grade $\mathrm{SrCl_2}$ (Merck) to which 0.2 mol % TlCl (pA grade from UCB) was added. No estimate of the actual concentration of thallium in the crystal was made. The samples were x-ray irradiated (tungsten anode, 50 kV, 50 mA) either at liquid-nitrogen temperature (LNT) or at room temperature, similar to previous experiments.[3] Before each irradiation the samples were routinely warmed up to 500 °C for 10 min and quenched to RT. The ESR measurements were performed at X-band frequencies, and a variable temperature accessory allowed measurements and pulse anneal experiments to be performed in the 8–300-K temperature range. To avoid optical bleaching effects, all experiments, except where otherwise stated, were performed under ambient red light.

III. RESULTS

A. ESR properties

Strong ESR transitions are observed below LNT after a short (typically 15 min) x-ray irradiation at LNT of the TlCl doped $\mathrm{SrCl_2}$ crystals (Fig. 1). They consist, besides transitions from the V_K (Refs. 16 and 17) and Tl^{2+} (Ref. 18) trapped hole centers, of a group of lines attributed to a $\mathrm{Tl}^0(1)$-type center, denoted as $\mathrm{Tl}_c^0(1)$. On the assumption that the observed linewidths ΔH stem from unresolved superhyperfine (shf) interactions, a reduced linewidth $\Delta H_{\mathrm{red}} = (g/g_0)\Delta H$ can be derived from the high-field resonance lines, which yields $\Delta H_{\mathrm{red}} = 3.9 \pm 0.4$ mT for this center.

In a sample, either x-ray irradiated at LNT followed by a warmup above 130 K or directly irradiated at RT, a second ESR spectrum can be observed (Fig. 2) attributed to another $\mathrm{Tl}^0(1)$-type center, named $\mathrm{Tl}_i^0(1)$. The low-field transitions exhibit a barely resolved splitting into two components corresponding to the two thallium isotopes $^{205}\mathrm{Tl}$ and $^{203}\mathrm{Tl}$, although the linewidths are close to those of the $\mathrm{Tl}_c^0(1)$ center [$\Delta H_{\mathrm{red}} = 3.5 \pm 0.4$ mT for $\mathrm{Tl}_i^0(1)$]. The isotope splitting of the low-field lines is larger for $\mathrm{Tl}_i^0(1)$ than for $\mathrm{Tl}_c^0(1)$, in agreement with the calculation on the basis of the ESR analysis presented in Sec. III B. The concentration of the $\mathrm{Tl}_i^0(1)$ center produced by x-ray irradiation in the dark does not change markedly by handling the specimens under white ambient light.

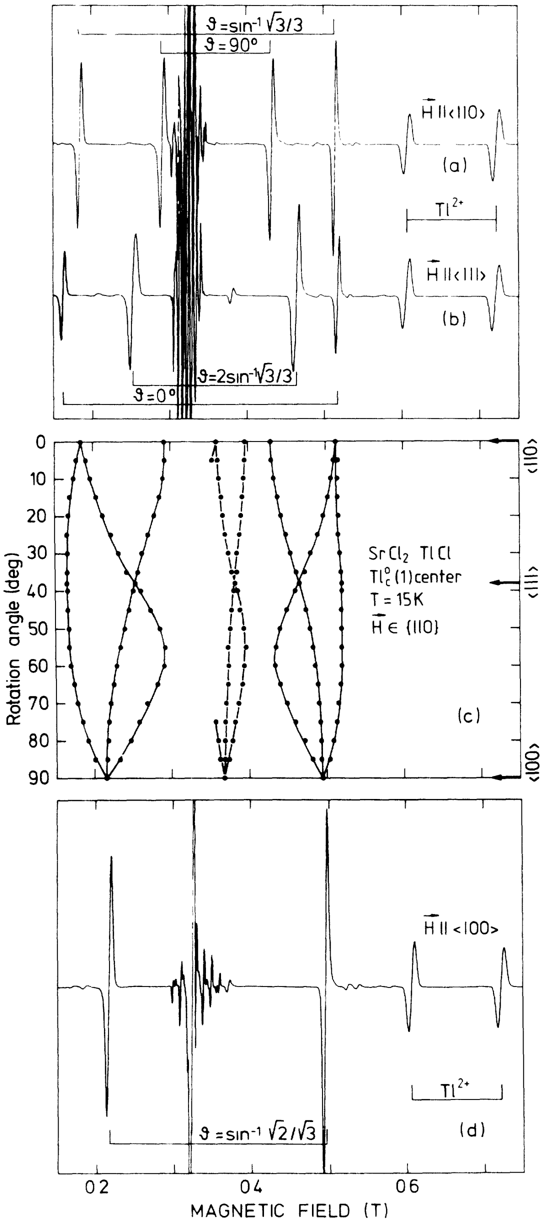

FIG. 1. ESR spectra measured at 15 K of the $\mathrm{Tl}_c^0(1)$ center in a $\mathrm{SrCl_2{:}TlCl}$ crystal x-ray irradiated for 30 min at LNT with (a) $\mathbf{H} \parallel \langle 110\rangle$, (b) $\mathbf{H} \parallel \langle 111\rangle$, (d) $\mathbf{H} \parallel \langle 100\rangle$, and (c) the angular variation in a $\{110\}$ plane.

An angular variation study of the ESR spectra with the magnetic field rotated in a {110} plane [Figs. 1(c) and 2(c)] shows that the spectra of both centers exhibit axial symmetry around ⟨111⟩ directions. Spectra are shown in Figs. 1(a), 1(b), 1(d), 2(a), 2(b), and 2(d), for the external static magnetic field **H** oriented along ⟨110⟩, ⟨111⟩, and ⟨100⟩, respectively. One recognizes the low- and high-field components originating from the strong hf coupling between the unpaired electron and the nuclear spins $I=\frac{1}{2}$ of the two thallium isotopes. The two thallium isotopes possess nearly equal nuclear magnetic moments, ${}^{205}\mu_I=1.6274$ and ${}^{203}\mu_I=1.6115$ nuclear magnetons, with corresponding natural abundances of 70% and 30%, respectively.[19]

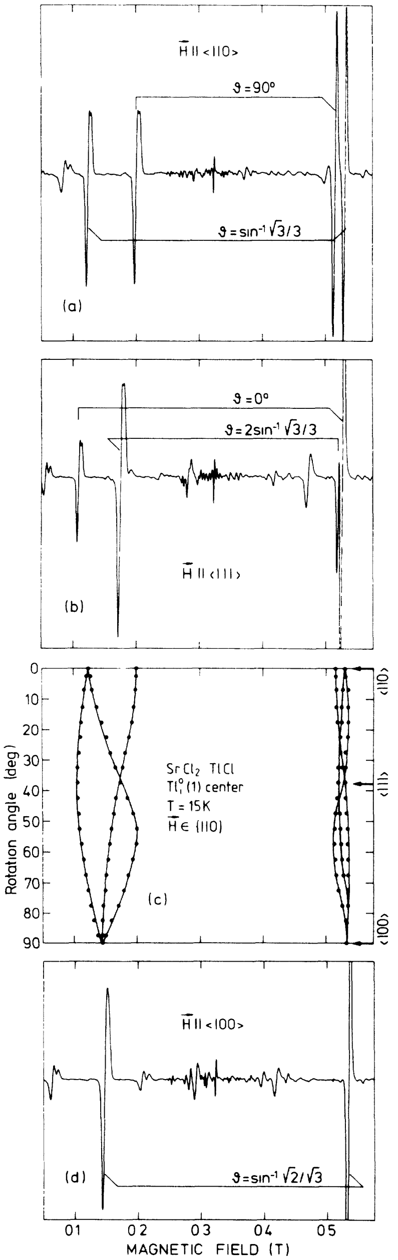

FIG. 2. ESR spectra measured at 15 K of the Tl^0_i(1) center in a SrCl$_2$:TlCl crystal x-ray irradiated for 20 min at LNT followed by a warmup to 140 K, with (a) **H** ∥ ⟨110⟩, (b) **H** ∥ ⟨111⟩, (d) **H** ∥ ⟨100⟩, and (c) the angular variation in a {110} plane.

The intensity of the ESR lines associated with the two Tl^0 centers increases with decreasing measuring temperatures. No saturation effects were observed at 15 K for microwave powers up to 50 mW. The linewidths are temperature independent in the 10–60-K range. Hence, it is concluded that if one of these Tl^0 defects possesses an internal reorientation motion in this temperature region, it is too slow to affect the ESR spectra. In fact, the models that we will propose in Sec. IV do not permit reorientation motions.

B. Analysis of the ESR spectra

The ESR spectra of both Tl^0_c(1) and Tl^0_i(1) centers are described by the following spin Hamiltonian (usual notation):

$$\frac{1}{g_0\mu_B}\mathcal{H} = \frac{1}{g_0}\left[g_\perp(H_xS_x + H_yS_y) + g_\parallel H_zS_z\right] + A_\perp(S_xI_x + S_yI_y) + A_\parallel S_zI_z \qquad (1)$$

with $S=\frac{1}{2}$ and $I=\frac{1}{2}$ and with the symmetry axes for the g and A tensors both parallel to the defect axis z ∥ ⟨111⟩.

For the Tl^0_c(1) center one observes, besides the normal allowed low- and high-field transitions, also other transitions that have become weakly allowed because of the very large hf anisotropy (Fig. 1). For each defect all the available line positions were fit to those calculated from (1) by means of a computer diagonalization and a least-squares fitting procedure. The results are presented in Table I for the most abundant ^{205}Tl isotope and for T=15 K. The calculated and experimental line positions agree to within 0.2 mT. The corresponding parameters for Tl^0(1) in KCl and RbCl are also given for comparison.

Theoretical expressions to second order for the g and A components have been derived before[20,21] and can be expressed in an axial approximation as

$$\Delta g_\parallel = g_0 - g_\parallel = \frac{\xi}{E}, \qquad (2)$$

$$\Delta g_\perp = g_0 - g_\perp = 2\frac{\xi}{E}\left(1+\frac{\xi}{E}\right), \qquad (3)$$

$$A_\parallel = \left(1-\tfrac{1}{2}\Delta g_\parallel\right)A_\sigma + \left(2+\tfrac{3}{2}\Delta g_\perp + \tfrac{1}{2}\Delta g_\parallel\right)\rho, \qquad (4)$$

$$A_\perp = \left(1-\tfrac{1}{2}\Delta g_\parallel\right)A_\sigma - \left(1+\tfrac{13}{4}\Delta g_\perp - \tfrac{9}{4}\Delta g_\parallel\right)\rho. \qquad (5)$$

In these expressions $\xi=5100\ \text{cm}^{-1}$ is the spin-orbit parameter of the Tl^0 p electron, E is the energy splitting induced by the crystal field and spin-orbit interactions between the ground and excited states originating from the $6p^1$ manifold. A_σ is the isotropic part of the hf interaction and includes both exchange polarization (dominant and negative for the free Tl^0 atom as it turns out) and

TABLE I. Spin Hamiltonian parameters determined at 15 K for the Tl^0(1)-type centers in SrCl$_2$:TlCl. The estimated experimental accuracy is 0.0005 for the g values, 0.2 mT for the A values, and 0.4 mT for the reduced linewidths. The corresponding parameters for the Tl^0(1) centers in KCl and RbCl are also given for comparison.

Center	$g_\parallel$	$g_\perp$	$A_\parallel$ [a] (mT)	$A_\perp$ [a] (mT)	ρ (mT)	A_σ (mT)	ΔH_{red} (mT)
Tl^0_c(1) in SrCl$_2$	1.8747	1.5609	+324.3	−95.8	+86	+95	3.9
Tl^0_i(1) in SrCl$_2$	1.8271	1.4536	+339.6	−189.0	+100	+54	3.5
Tl^0(1) in KCl[b]	1.7892	1.3077	+372.2	−201.1	+97	+76	2.7
Tl^0(1) in RbCl[c]	1.760	1.228	+342.7	−246.8	+97	+27	1.7

[a] Choice of signs is discussed in Refs. 3, 11, 21, and 22.

[b] From Ref. 3.

[c] From Ref. 26.

a positive Fermi-contact contribution caused by s mixing if the Tl^0 atom happens to be positioned in a crystal field with a strong odd component.[11,22] The anisotropic part of the hf tensor is $\rho = \frac{2}{5}(\mu_I/I)\langle r^{-3}\rangle_{6p}$, which is an atomic property much less influenced by the nature of the crystal field, and which should be more or less constant for various Tl^0 defects. It has been remarked that the foregoing hf expressions, when applied to analyze the experimental data, give remarkably consistent and convincing ρ and A_σ values[11-13,21-23] for all np^1 ($n = 4, 5, 6$) heavy-metal defects observed so far. The numerical values of ρ and A_σ resulting from such an analysis applied to the present data are given in Table I together with the corresponding numbers for the Tl^0(1) center in KCl and RbCl. The implications of these values will be discussed in Sec. IV.

C. Production properties

Pulse annealing experiments were performed in order to identify possible correlations between the production and decay of the Tl^0(1) centers in SrCl$_2$ on the one hand, and mobilities of holes and anion vacancies on the other hand. As shown in Fig. 3 the Tl^0_c(1) centers are readily produced by x-ray irradiation at 77 K, together with V_K and Tl^{2+} trapped hole centers. Further pulse annealing results in a partial decay of the V_K centers accompanied by an increase in the concentration of Tl^{2+} centers and a small decrease in the concentration of Tl^0_c(1) centers. These variations in concentration are attributed to the trapping of holes from V_K centers, which become mobile in this temperature range,[24] by substitutional Tl$^+$ ions, forming Tl^{2+}, and by Tl^0_c(1) centers, transforming back into the initial precursor.

A further decay of the Tl^0_c(1) centers, accompanied by an increase in the concentration of Tl^{2+} centers above this temperature, seems to be due to further trapping of holes. However, the decay of the V_K centers cannot be completely followed in the ESR spectra because of overlap with the transitions attributed to V_{KA} centers, which are formed in the same temperature range.[24]

Above 130 K the decay of the Tl^0_c(1) centers correlates with the appearance and growth of the ESR lines attributed to the Tl^0_i(1) centers. The latter reach maximum concentration at 170 K, where the Tl^0_c(1) have vanished. This behavior suggests a transformation of the Tl^0_c(1) into Tl^0_i(1) centers. In this process the incipient mobility of the anion vacancy seems to play a role. Indeed above 130 K the production of M centers has been observed[25] in SrCl$_2$, as well as changes in the shf structure of the Tl^{2+} centers[18] formed by x-ray irradiation at 77 K. A study of Pb^{2+}-doped SrCl$_2$ crystals, which will be presented in a forthcoming paper, demonstrates that Pb$^+$ centers of the laser-active-type structure are formed in the same temperature region. All these processes can be correlated to the onset of anion vacancy movement in the SrCl$_2$ crystal.

Changes in the concentration of both Tl^0_i(1) and Tl^{2+}

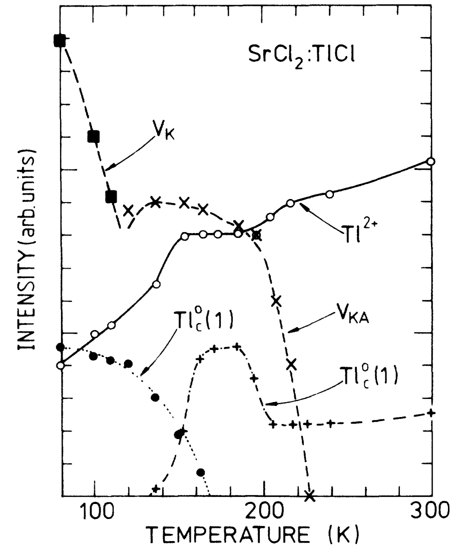

FIG. 3. Thermal growth and decay of the two Tl^0(1)-type centers in a SrCl$_2$:TlCl crystal x-ray irradiated for 30 min at LNT. The intensity of the ESR lines was measured at 60 K for **H** ∥ ⟨111⟩, after an anneal of 3 min to the indicated consecutive temperatures above LNT. The variation of the relative intensities of the ESR lines attributed to the V_K, V_{KA}, and the Tl^{2+} centers are also presented. After the anneal at 240 K the sample was briefly warmed up to RT and measured again at 60 K.

centers are also taking place above 190 K (Fig. 3). These are associated with the decay of the V_{KA} centers, which apparently lose their holes at this temperature and have disappeared completely by 230 K.

Further information concerning the $\mathrm{Tl}_c^0(1)$ centers comes from isothermal production experiments. As drawn in Fig. 4, the formation rates of the $\mathrm{Tl}_c^0(1)$ and Tl^{2+} centers under x-ray irradiation at LNT are similar, which suggests that simple electron trapping and hole trapping, respectively, are involved in their production.

IV. MODELS OF THE $\mathrm{Tl}^0(1)$ CENTERS IN SrCl_2

The analysis of the hf parameters, and, in particular, the resulting sign of the isotropic part A_σ, has consistently proved to be a very reliable test for the presence or absence of an odd crystal field in the microscopic models of the np^1 ($n = 4,5,6$) heavy-metal ion centers.[11–13,21–23] A comparison of the spin-Hamiltonian parameters of the two $\mathrm{Tl}^0(1)$ species in SrCl_2:TlCl crystals with the corresponding parameters of the $\mathrm{Tl}^0(1)$ centers observed in various alkali-metal halides, suggests already that both centers are likely of the $\mathrm{Tl}^0(1)$ type, i.e., essentially consisting of a Tl^0 atom with a negative-ion vacancy in its immediate neighborhood. This structural model is supported by the analysis of the hf parameters with formulas (4) and (5), the results of which are presented in Table I. Because Tl^0 atom defects in even crystal fields possess large negative A_σ values [as low as -190 mT (Refs. 11 and 22)], there is no doubt that the positive values for $\mathrm{Tl}_c^0(1)$ and $\mathrm{Tl}_i^0(1)$ in Table I originate in both cases from a substantial s mixing whose positive contribution overpowers the negative exchange polarization contribution. This s mixing can only be caused by the presence of an odd crystal field.

The proposed models of $\mathrm{Tl}_c^0(1)$ and $\mathrm{Tl}_i^0(1)$ consistent with the ESR analysis and production properties are presented in Fig. 5. For $\mathrm{Tl}_c^0(1)$ the model consists of a substitutional Tl^0 atom on a cation site associated with a NN anion vacancy along a $\langle 111\rangle$ direction [Fig. 5(a)]. This anion vacancy is the original charge compensating one for the substitutional Tl^+ ion before electron trapping. In the model for the $\mathrm{Tl}_i^0(1)$ center [Fig. 5(b)] the Tl^0 atom now occupies the empty interstitial site of the fluorite lattice and is associated in a linear configuration along a $\langle 111\rangle$ direction with a anion-cation divacancy, the anion vacancy being closest to the Tl^0. Within the framework of these models the production of $\mathrm{Tl}_i^0(1)$ from $\mathrm{Tl}_c^0(1)$ involves a $\langle 111\rangle$-directed jump of the Tl^0 atom away from its cation site through the adjoining anion vacancy towards the empty interstitial site. The fact that this transformation occurs at temperatures where the anion vacancy becomes mobile (130 K) may not be accidental. For some subtle reason the incipient mobility of the anion vacancy around the Tl^0 may induce this jump.

Additional evidence for the mutual consistency of these models comes from a closer inspection of the magnitude of the isotropic hf interaction parameter A_σ. Indeed, the decreasing anion-cation distances in the series SrCl_2 (0.302 nm), KCl (0.315 nm), and RbCl (0.329 nm) suggest a decreasing strength of the odd crystal field experienced by the Tl^0 atom, and indeed there is a pronounced decrease of A_σ in going from $\mathrm{Tl}_c^0(1)$ to $\mathrm{Tl}^0(1)$ in KCl and RbCl in that order (see Table I). Also, the g parameters tend to increase in the direction of the free electron g value for increasing strength of the crystal field. A similar behavior has been observed for the isoelectronic Pb^+ center throughout the CaF_2, SrF_2, and BaF_2 series.[13]

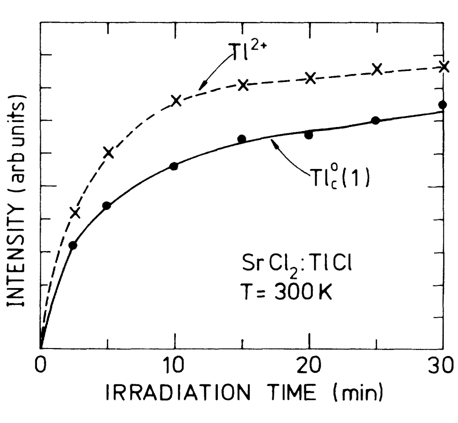

FIG. 4. Isothermal production at LNT of the $\mathrm{Tl}_c^0(1)$ and Tl^{2+} defects in SrCl_2:TlCl as a function of x-ray-irradiation time. The relative intensities of the ESR lines measured at 60 K for **H** || $\langle 111\rangle$ are presented.

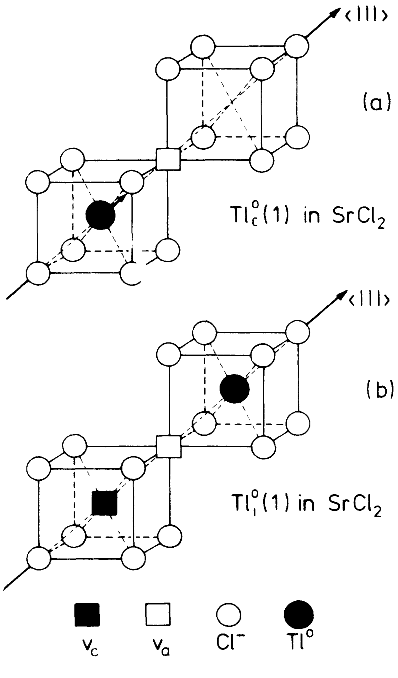

FIG. 5. Proposed structures of the $\mathrm{Tl}_c^0(1)$ and $\mathrm{Tl}_i^0(1)$ centers in SrCl_2 as inferred from the ESR measurements in this paper.

In the $\mathrm{Tl}_i^0(1)$ center the effect of the NN anion vacancy charge should be reduced by the charge of the adjoining cation vacancy. One expects a reduced odd crystal field acting on the Tl^0 in this case with a resulting reduction in A_σ, and decrease of the g values. This, as Table I shows, is indeed observed. Finally, in both models the Tl^0 atom is surrounded by a cube of chlorine ions. These very similar surroundings are consistent with the very close values of the reduced linewidths (see Table I), which would then mainly result from shf interactions with the chlorine nuclei.

Another structural model, i.e., the Tl^0 occupying the anion site and flanked by a NN cation vacancy along a $\langle 111 \rangle$ direction must be rejected. The double-negative charge of the cation vacancy would prohibit the ground-state p-electron orbital of the Tl^0 atom to be oriented along a $\langle 111 \rangle$ direction. Rather, it would push the ground state into a plane perpendicular to that direction, and this would result in a center whose symmetry is not compatible with the observed axial symmetry along $\langle 111 \rangle$, observed for both centers.

V. CONCLUDING REMARKS

The two $\langle 111 \rangle$-oriented $\mathrm{Tl}^0(1)$ centers, called $\mathrm{Tl}_c^0(1)$ and $\mathrm{Tl}_i^0(1)$, have been shown to possess the laser-active structure: The core of the structure is in both cases a Tl^0 atom perturbed by a NN anion vacancy, but the Tl^0 atom is located in a substitutional cation position, and in the energetically more favorable interstitial position of the fluoride lattice, respectively. Apart from the study of the production properties, the analysis of the isotropic part of the hf interaction has again proven to be very powerful in identifying the microscopic structure and in differentiating between the models for the two defects. A defect structure involving an even crystal field would be expected for a defect with a structure analogous to the $\mathrm{Tl}^0(2)$ center in KCl.[3] Although the stabilization of an additional anion vacancy by the effectively positive $\mathrm{Tl}_c^0(1)$ center would be plausible, the absence of Tl^0 spectra with the signature of an even crystal field ($A_\sigma \approx -190$ mT) indicates that this process is much less effective than the site-switching process leading to $\mathrm{Tl}_i^0(1)$. Finally, no indication is found for Tl^0 atoms on a negative-ion site—a genuine site-switched Tl^0 center such as found in the alkali halides[11]—which is possible in view of its electrical neutrality. It shows that this position is unstable with respect to a jump of the atom into the interstitial site.

Our measurements also establish that at least part, if not all, of the substitutional Tl^+ dopant is substitutional and charge compensated by an adjoining anion vacancy along $\langle 111 \rangle$. This is analogous to the charge compensation of divalent cations in alkali halides by a cation vacancy, taking into account the sign reversal of the effective charges. The present paper also confirms that the anion vacancy becomes mobile in $\mathrm{SrCl_2}$ above 140 K, and our results indicate that the thermal conversion of $\mathrm{Tl}_c^0(1)$ to $\mathrm{Tl}_i^0(1)$ at and above this temperature may be helped by the incipient mobility of the anion vacancy.

Although both centers possess the laser-active structure, it is by no means established that they are in fact suitable laser centers. Their optical absorption and luminescence properties should be carefully investigated. There is a good motivation to do so: Based on our ESR measurements the concentration of both $\mathrm{Tl}^0(1)$-type centers in $\mathrm{SrCl_2}$ is one to two orders of magnitude larger than the maximum concentration of $\mathrm{Tl}^0(1)$ centers in KCl crystals doped with 2 mol % TlCl. The latter crystal has been the most dependable laser material so far. The higher thermal stability of the $\mathrm{Tl}_i^0(1)$ (up to 370 K) compared to $\mathrm{Tl}_c^0(1)$ could favor the former. However, thermal stability is not the only concern: A high quantum efficiency for the luminescence process, stability under laser pump excitation and the absence of excited-state absorption at the lasing wavelength, are equally important. This is illustrated by the work on the $\mathrm{Tl}^0(1)$ defect, which can be produced in virtually all the alkali-metal halide crystals of the rocksalt structure: Only the $\mathrm{KCl{:}Tl}^0(1)$ laser has proven to be stable and dependable.

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