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Brief Reports

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ESR results on the laser-active $\mathrm{Tl}^0(1)$ centers in RbCl and KBr

S. V. Nistor,* E. Goovaerts, A. Bouwen, and D. Schoemaker
Physics Department, University of Antwerp (Universitaire Instelling Antwerpen), B-2610 Wilrijk, Belgium

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The ESR spectra, the production, and some optical excitation properties of the laser-active $\mathrm{Tl}^0(1)$ centers in Tl^+-doped KBr and RbCl are discussed. The g values and hyperfine components are comparable to the KCl data obtained in an earlier paper but the linewidths are much larger (16 mT vs 2.7 mT). One concludes that the amount and the nature of the delocalization of the $\mathrm{Tl}^0\,6p$ electron is similar to that in KCl. These results correlate well with the optical absorption and luminescence data, which do not vary drastically for $\mathrm{Tl}^0(1)$ among all the alkali halides.

Recently the structure of several complex thallium atom centers produced by ionizing radiation in $\mathrm{KCl{:}Tl}^+$ were derived from a detailed electron-spin-resonance (ESR) investigation.[1] These centers were called $\mathrm{Tl}^0(1)$ and $\mathrm{Tl}^0(2)$ and both possess tetragonal symmetry around $\hat{z}\,||\,[100]$. In $\mathrm{Tl}^0(1)$ a Tl^0 on a cation site is perturbed by a single adjoining anion vacancy, whereas in $\mathrm{Tl}^0(2)$ the Tl^0 is flanked by two such vacancies (hence the numbers 1 and 2 between parentheses). Results on identical centers in Ga^+- and In^+-doped KCl have also been reported.[2,3]

The $\mathrm{Tl}^0(1)$ center has been shown since to be an attractive laser active center providing stable cw or picosecond pulse outputs of hundreds of mW or more between ~1.3 and ~1.9 μm in various alkali halides at room temperature.[4-6] The odd crystal field induced by the single anion vacancy is essential here because it makes transitions between the crystal-field- and spin-orbit-split multiplets of the Tl^0 ground state modestly allowed.[7] This is particularly true for the 1050-nm transition which is suitable for pumping with a neodymium-doped yttrium aluminum garnet laser. Both the Tl^+ and the anion vacancy have a strong affinity for electrons, and joined together, as they are in the $\mathrm{Tl}^0(1)$ center, they stabilize an electron in a neutral defect which is both optically and thermally (up to 400 K) very stable.

We have searched for the $\mathrm{Tl}^0(1)$ ESR spectra in Tl^+-doped NaCl, RbCl, and KBr. In our $\mathrm{NaCl{:}Tl}^+$ samples the x irradiation produces numerous and complex ESR spectra which we have not yet completely analyzed. A common problem in NaCl crystals grown from reagent grade material is the occurrence of ESR lines of several complex Fe^+ centers.[8] Clearly, Fe^{2+} ions are common impurities in NaCl and they compete with the Tl^+ as traps for electrons. In KBr and RbCl the $\mathrm{Tl}^0(1)$ spectra could be distinguished and the results are presented here. These crystals were grown by the Bridgman-Stockbarger technique. In order to eliminate the anionic impurities, oxygen and OH^- ions in particular, the following purification procedure was used.[9] First, a fused silica ampoule containing Suprapure (Merck) alkali halide powder and 2 mol% of Ultrapure (Ventron) TlCl was heated to +250 K under a vacuum of 10^{-3} mm Hg. Subsequently, the pumping was discontinued and the powder was flushed with argon gas containing $\mathrm{CCl_4}$ vapor while the temperature was raised unitl the powder melted. The ampoule was then sealed off and the crystal was carefully grown. The crystals possessed high optical quality. About 2 mol% of TlCl or TlBr was added to the melt and about 0.2 mol% is believed to be actually in the samples.

Similar to $\mathrm{KCl{:}Tl}^+$ the $\mathrm{Tl}^0(1)$ ESR spectra can be observed in $\mathrm{RbCl{:}Tl}^+$ and $\mathrm{KBr{:}Tl}^+$ after 1- or 2-h x irradiation at 250 K.[1] The lines are very broad (~16 mT) which means that they appear weak and that Tl isotope effects are not resolved. An angular variation in a {100} plane (Fig. 1) confirms the axial behavior of the ESR spectra in agreement with the tetragonal symmetry around ⟨001⟩ of the $\mathrm{Tl}^0(1)$ center. The spectra were fitted to an axial spin-Hamiltonian comprising a Zeeman and a hyperfine (hf) term.[1] The resulting components of the g tensor ($\overleftrightarrow{g}$) and the thallium hyperfine tensor ($\overleftrightarrow{A}$) are given in Table I

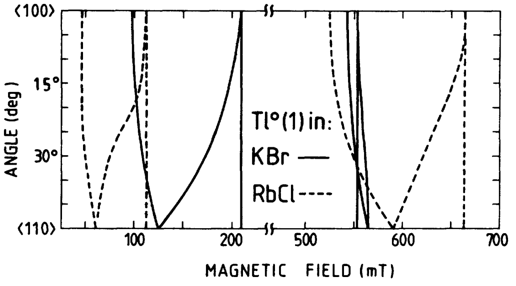

FIG. 1. Angular variation in a {100} plane of the ESR spectra of $Tl^0(1)$ in RbCl (– – –) and KBr in (——) at 13 K. The microwave frequency is $\nu = 9.21$ GHz.

together with the KCl data.[1]

The g shifts are comparable in the three crystals showing that the crystal-field contributions to the splitting of the Tl^0 ground state are similar. This is confirmed experimentally[4–6]: The pumping transitions are at 1050 nm in KCl and at 1100 nm in RbCl and KBr. The Stokes-shifted luminescence, which is determined by the relaxed excited state, is centered near 1.5 μm in KCl and RbCl and at 1.6 μm in KBr.

The $Tl^0(1)$ hf components whose signs were determined earlier[1–3] exhibit the property that $|A_{\parallel}| > |A_{\perp}|$, in contrast to, e.g., the $Tl^0(2)$ center[1] for which $|A_{\parallel}| < |A_{\perp}|$. The essential reason underlying the latter relation is that for the np ($n = 4,5,6$) atoms and ions both in the free state or in environments possessing reflection symmetry the isotropic contribution to the hf components is negative and large.[1–3] For $Tl^0(1)$ the odd crystal field supplied by the anion vacancy mixes an appreciable amount of s character into the ground state. The resulting contribution to the isotropic hf interaction dominates the intrinsic negative one and making it, in fact, positive (see Table VI in Ref. 2), hence the relation $|A_{\parallel}| > |A_{\perp}|$ for $Tl^0(1)$. Because the hf components are similar in the three crystals it is concluded that the magnitude of the odd crystal-field component induced by the anion vacancy is very comparable. The hf components are, in fact, quite sensitive to the size of the odd crystal field. This implies that delocalization of the $Tl^0(1)$ np electron towards the surrounding lattice is comparable in the three crystals.

The ESR linewidth of $Tl^0(1)$ is determined by two factors.[1] There is first the preferential superhyperfine (shf) interaction with the nucleus of the nearest-neighbor halogen ion along ⟨001⟩. Both Cl and Br have nuclear spin $\frac{3}{2}$ and a four-line shf structure results. This structure is not resolved because each of these components is broadened by the fact that the $Tl^0(1)$ center $6p$ electron exhibits a certain amount of delocalization. In Refs. 1–3 it was argued that the delocalization was exclusively towards the perturbing anion vacancy giving $Tl^0(1)$ a sizable amount of F-center character, ~40%, in fact. Using 40% of the F-center linewidths[10] one can reproduce the $Tl^0(1)$ center linewidths in Table I by accepting a shf interaction with the Cl nucleus of about 0.8 mT in RbCl and KCl and of about 5.0 mT with the Br nucleus in KBr. These numbers are not unreasonable, the larger Br shf interaction reflecting primarily its larger nuclear moment. However, the simple hf scaling argument used in Refs. 1–3 may be subject to criticism. Furthermore, the success obtained in Ref. 7 in explaining the $Tl^0(1)$ center optical absorption by means of a simple crystal-field calculation implies either a much lower delocalization towards the anion vacancy and/or a more diffuse one in which the Tl^0 $6p$ wave function extends over two or more shells of surrounding ions. Settling the question of the extent and nature of the delocalization awaits the application of more powerful experimental tools and theoretical analyses. The results obtained for $Tl^0(1)$ in one alkali halide may very well be typical for most of the alkali halides.

TABLE I. The spin-Hamiltonian parameters of the $Tl^0(1)$ centers in several alkali halides. The hyperfine parameters ($\overleftrightarrow{A}$) and the linewidth ΔH are given in mT.

	$g_{\parallel}$ [001]	$g_{\perp}$	$A_{\parallel}(Tl)$[a] [001]	$A_{\perp}(Tl)$[a]	ΔH
$KCl:Tl^+$[b]	1.7892	1.3077	+372.2	−201.1	2.7
	±0.0007	±0.0005	±0.4	±0.2	±0.5
$KBr:Tl^+$	1.778	1.345	+352.4	−186.6	16
	±0.002	±0.002	±0.8	±0.8	±1
$RbCl:Tl^+$	1.760	1.228	+342.7	−264.8	17
	±0.002	±0.002	±0.8	±0.8	±1

[a] For KCl hyperfine components correspond to ^{205}Tl; for RbCl and KBr they represent some average for ^{205}Tl and ^{203}Tl because isotope effects are not resolved, but the average is strongly weighed towards ^{205}Tl.

[b] From Ref. 1.

As is the case in KCl the Tl^0(1) concentration in RbCl and KBr can be enhanced by ~20% through an optical F-center excitation at 250 K following the x irradiation at this temperature.[1] It was shown that this happens because the freed electrons are trapped by Tl$^+$(1) centers[1], i.e., the precursor centers of Tl^0(1). However, much larger gains amounting to a factor of 3 can be obtained by employing the simple procedure for optimizing the laser samples[6]: The sample at 250 K is subjected to bleaching by a white light source (60-W halogen lamp). It is also observed that the enhancement is higher when the Tl$^+$ concentration is higher, though this effect levels off with concentration.

From the point of view of laser operation the white light excitation produces several desirable things: It strongly reduces the amount of ⟨110⟩-oriented Tl$_2{}^+$ dimer centers,[11] while at the same time strongly enhancing the Tl^0(1) concentration. [The number of Tl^0(2) is also strongly reduced[1] but they are not produced anyway in the more heavily Tl$^+$-doped crystals.] Tl$_2{}^+$ has strongly allowed transitions at 460, 860, and 1760 nm.[11] The white light excitation produces mobile electrons from ionizing the Tl$_2{}^+$ and the F centers (at 540 nm) and mobile anion vacancies from the ionized F centers. These electrons and vacancies can then be trapped by the Tl$^+$ impurities contributing sizably to the Tl^0(1) enhancement.

In our experiments the maximum amount of Tl^0(1) was reached after 5 min of white light excitation in KCl, 1 min in RbCl, and about 30 sec in KBr. From then on the light excites the weakly allowed Tl^0(1) transitions,[4,12] breaking down its concentration. The latter process was faster in those samples in which the Tl^0(1) increase was also faster. For instance, in KBr the Tl^0(1) drops by 50% after an additional excitation of 1 min, while only 20% of Tl^0(1) is lost in KCl after 8 min of white light. Clearly, the optimalization of Tl^0(1) concentration for laser operation will require individual study in the various alkali halides.

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[*] Permanent address: Central Institute of Physics, C.P. MG-7, Magurele-Bucuresti, 76900 Roumania.

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