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IDENTIFICATION OF $Tl^0(1)$ PERTURBED CENTERS BY EXCITED STATE OPTICAL ABSORPTION TECHNIQUE*

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ABSTRACT

The $Tl^0(1)$ center consists of a Tl neutral atom in a substitutional site perturbed by an adjacent anion vacancy in an alkali halide crystal. These centers are laser active, being efficiently pumped by Nd lasers, emitting in a broad band peaking at 1.52 µm. In order to produce these centers it is necessary to grow single crystal with a concentration of tenths of mol per cent of Tl in the crystal. Due to the high vapor pressure of this dopant, one alternative is to grow them by the Bridgman technique. The problem with this method is that the thermal gradient in the boule is rather high, inducing formation of Tl dimers that affect the laser performance of these centers. By using a pump probe technique we were able to identify, in the KCl crystals grown by the above described method, the usual transitions of the $Tl^0(1)$ center and also one band peaking at 680 nm that we attribute to the strongly allowed excited state absorption of the $Tl^0(1)$ perturbed specie. Besides, we observed a strong transition band peaking at 800 nm that can be attributed to an energy transfer mechanism between the $Tl^0(1)$ and Tl^+_2 centers.

1. INTRODUCTION

Color centers and transition metal ions in ionic crystals have shown a great potential as candidates for tunable lasers sources. One of these centers, the $Tl^0(1)$ defect, particularly in KCl crystals, is a well established laser medium[1]. They are produced by irradiation of Tl^+ - doped KCl crystals and were identified by electron paramagnetic resonance (EPR) and optical absorption studies as a substitutional Tl atom strongly perturbed by the field of an adjacent anion vacancy[2,3] (figure 1). An accurate determination of the absorption bands was obtained by tagged absorption experiments[4], by tagged magnetic circular dichroism (MCD)[5], and by optically detected magnetic resonance (ODMR)[5], establishing the three low lying optical transitions in KCl at 1040, 720 and 550 nm. The optical transitions[4] were properly described by a simple model of a neutral Tl atom perturbed by an axial crystal field due to a neighboring anion vacancy. The Tl atom consists of a single valence 6*p* electron outside closed shells, thus in the free atom the ground and first excited levels are $6p^2P_{1}/_{2}$ and $6p^2P_{3}/_{2}$, respectively, separated by a spin-orbit splitting of nearly 8000 cm^{-1} (see fig. 1). In the color center the (odd) field of the defect is responsible for: (1) the splitting the *p* manifold levels into three Kramer's doublets, and (2) the mixing of substantial amounts of higher-lying even-parity states, which is very important for the laser activity. This mixing allows electric dipole transitions of modest oscillator strength between the *p* manifold components. The laser transition is the lowest energy transition, whose emission properties (f= 0.0075 and half - power band width = 650 cm^{-1}) imply in a gain cross section of 1.3 x $10^{-17}cm^2$. It should be noted that the absorption band of the laser transition, which peaks at 1040 nm and is about 1300 cm^{-1} wide, overlaps the 1040 nm wavelength of the Nd:YAG laser used as the pump source.

Due to the mechanism of center formation[4], several other aggregates are also formed. Two of the additional centers were identified by electron spin resonance (ESR)[5] as Tl dimer centers. In one of then, two Tl^+ ions on adjacent cation sites share an unpaired electron , thus forming a Tl_2^+ molecular center[6] (figure 2). The other one , also identified by ODMR experiments[7], consists of two adjacent Tl^+ ions around one anion vacancy, sharing one unpaired electron (figure 2). This Tl^+ perturbed $Tl^0(1)$ denoted Tl_2^0 (1) center. The optical absorption and emission properties of the $Tl_2^0(1)$ center are also very similar to those of the $Tl^0(1)$ defect. Therefore it was suggested that the unpaired electron, which is mainly in a $6p_z$, orbital along the line connecting the Tl^+ ions and the anion vacancy, is hopping (or tunneling) between two $Tl^0(1)$ - like configurations.

2. EXPERIMENTAL

Tl:KCl crystals were grown by static Bridgman method[8]. The final Tl concentration was in the range of 0.2 up to 0.3 mol %, measured by spectrographic methods. Good optical quality samples were obtained by choosing the central part of the boule and residual thermal stress could be eliminated by thermal annealing the samples. Samples with 2 x 10 x 10 mm³ were cleaved, polished and electron irradiated at 77 K. The irradiation was performed in a Dynamitron accelerator (1.5 MeV, 28 μA x min./cm²). During the irradiation the samples were placed in a copper boat floating in liquid nitrogen. F centers densities of $10^{18} cm^{-3}$ were obtained in this way. The usual photoconverting process of shining white light at -30°C was used to ionize the F centers, with the mobile vacancy getting attached to the Tl^+ and then capturing the electron. Optical densities of 0.5 at the peak of the absorption band were obtained as shown in figure 3. The typical absorption bands of the $Tl^0(1)$ center are clearly shown (bands peaking at 1040 nm and 550 nm) and the 720 nm band, that is much weaker than the former two. The band peaking at 460 nm is typical of the Tl_2^+ centers[6], in spite of the proximity of the K band of the F centers[9]. The band peaking at 635 nm is attributed to a $Tl^0(1)$ center perturbed by a Tl^+ ion, the $Tl_2^0(1)$[7]. Besides this absorption band, this center shows two other bands, one peaking at 800 nm and a weaker one peaking at 1070 nm. The band at 800 nm is also due to F_2 color centers. By exciting the crystal with 1.064 μm laser light it was observed one sole emission centered at 1.52 μm, corresponding to the laser transition of the $Tl^0(1)$ center. The decay time was measured by the phase-lag method providing the expected 1.6 μs.

The excitation spectrum (figure 4) is taken by fixing the emission wavelength at 1.52 μm. It shows the expected lower lying $Tl^0(1)$ centers absorption bands (1040 nm, 720 nm and 550 nm) and also a band peaking at 635 nm. It is known[7] that the $Tl_2^0(1)$ centers emit a band peaking at 1.45 μm, therefore overlapping the monitoring wavelength. Due to this overlapping, the presence of this centers is clearly seen by the strongest absorption band peaking at 635 nm. In order to investigate more carefully the presence of other Tl species, we used a pump-probe technique (tagging). The pump beam is a modulated 1.064 μm laser line that produces first and ground state time dependent populations. These populations are then probed by measuring the transmission of a secondary probe light. Transitions from the ground and first excited states are positive and negative respectively. Figure 5 shows the excited state absorption spectrum. The typical $Tl^{0}(1)$ bands peaking at 550 nm and 620 nm ($\Phi \rightarrow \Sigma$, $\Psi \rightarrow \Sigma$) are clearly seen. The band corresponding to an excited state absorption peaking at 680 nm is seen for the first time.

As it is shown by ODMR[7], the energy level diagram of the Tl_2^{0} (1) center is very similar to the $Tl^{0}(1)$ center, and also the strength of the transitions. Therefore we might expect strong transition probabilities of the $\Phi \rightarrow \Sigma$ and also $\Psi \rightarrow \Sigma$ (excited state transition), as it is found in the $Tl^{0}(1)$ counterpart. It should be noticed that there is a direct absorption band peaking at 635 nm ($\Phi \rightarrow \Sigma$) that is attributed to the $Tl_2^{0}(1)$ center, so the 680 nm band is due to these centers that are $Tl^{0}(1)$ alike and correspond to the $\Psi \rightarrow \Sigma$ transition.

The excited state absorption band peaking at 800 nm is probably due to Tl_2^{+} centers. These centers show a broad absorption band peaking at 1.76 μm that absorbs fairly well the emission of the $Tl^{0}(1)$ centers, therefore presenting a modulated population of the first excited and the ground state, accounting for the excited state transition observed at 800 nm (figure 5). Samples that were annealed to 700°C for 15 minutes and quenched to room temperature have not shown the presence of these aggregates as can be seen in figure 6.

3. *CONCLUSIONS*

In spite of the absence of pronounced absorptions bands of $Tl^{0}(1)$ perturbed centers [$Tl_2^{0}(1)$] in the direct spectrum, we could clearly identify by the excitation and excited state spectra the presence of $Tl_2^{0}(1)$ centers. Besides, the Tl_2^{+} centers that show a modest oscillator strength (f= 0.021) at the fundamental transition (1.76 μm) undetected in the direct absorption spectrum, were clearly identified by the 460 nm strong absorption band (f= 0.36)[10], that shows a significant modulation due to the $Tl^{0}(1)$ center emission, giving raise to the observed 800 nm band. These results show clearly that it is of fundamental importance the growth method and Tl concentration on lasers samples due to interfering species. Annealing and quenching of these samples could eliminate the aggregation problem.

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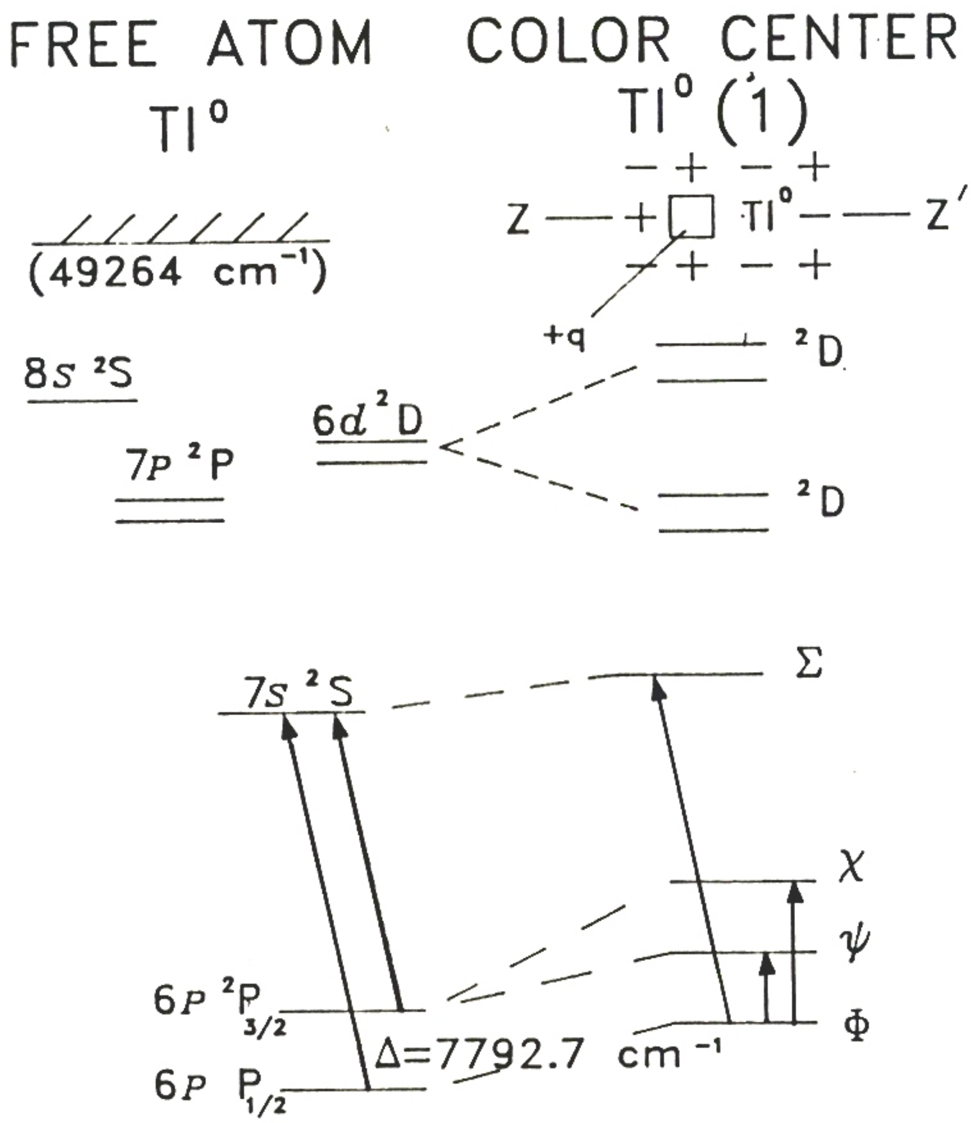

FIGURE 1. Energy levels of atomic thallium (left) and of the $Tl^{0}(1)$ color center (right). The states labeled Φ, Ψ and X have mainly a 6p character, while the Σ state is mainly derived from 7s. The Φ and Ψ states contain significant admixture of the Σ state.

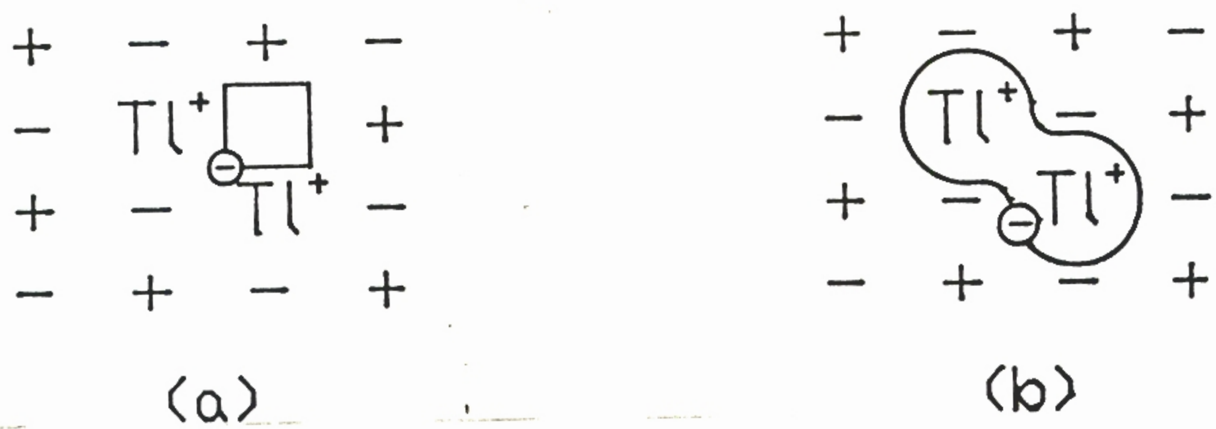

FIGURE 2. Schematic representation of the $Tl_2^0(1)$ (a) and Tl_2^+ (b) centers. The $Tl_2^0(1)$ consists of two Tl^+ cations around one anion vacancy, sharing one unpaired electron. The Tl_2^+ molecular center involves two Tl^+ ions on adjacent cation sites sharing an unpaired electron.

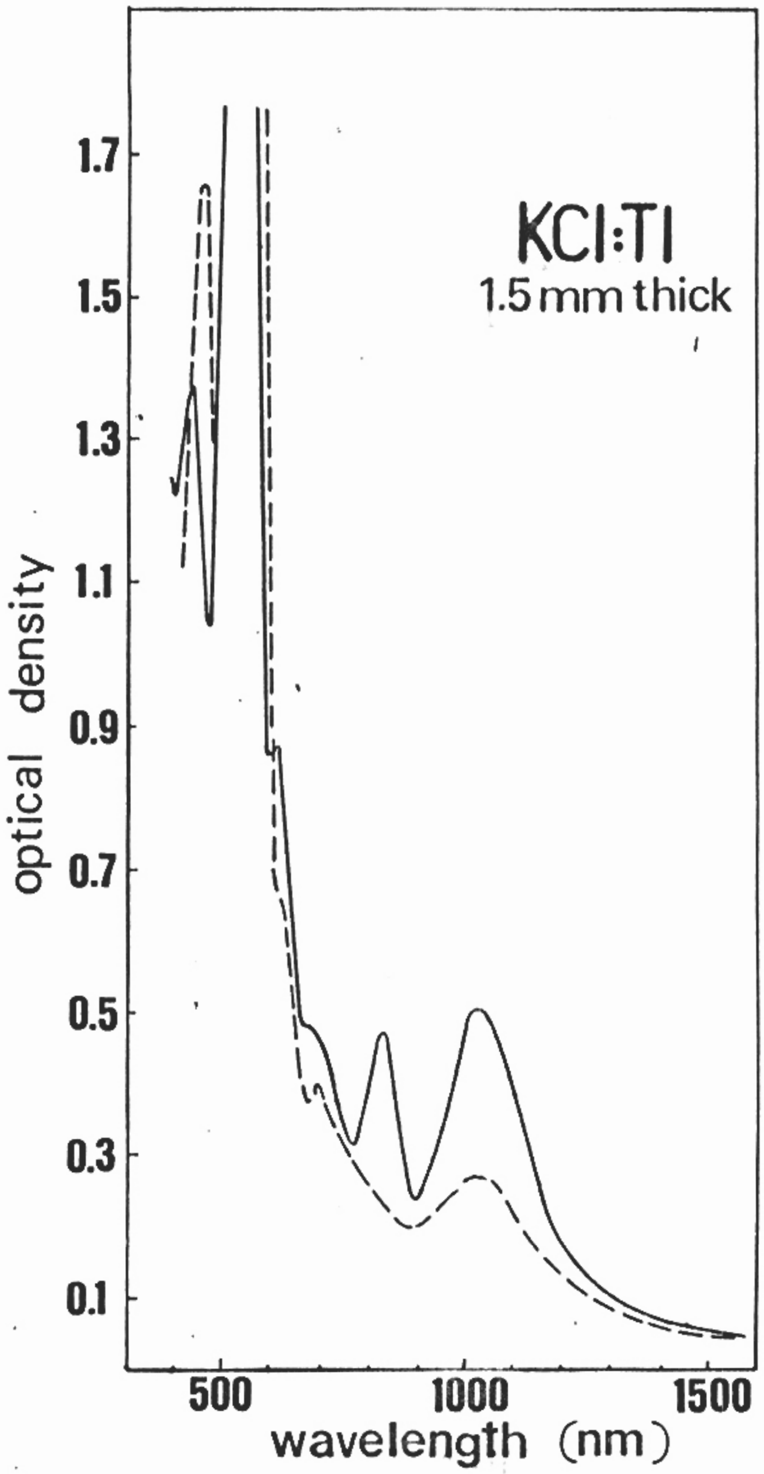

FIGURE 3. Absorption spectrum of a radiation-damaged KCl:Tl crystal at 77 K. The dashed line presents the spectrum after electron bean irradiation and the solid curve shows the spectrum after the photoconverting processes.

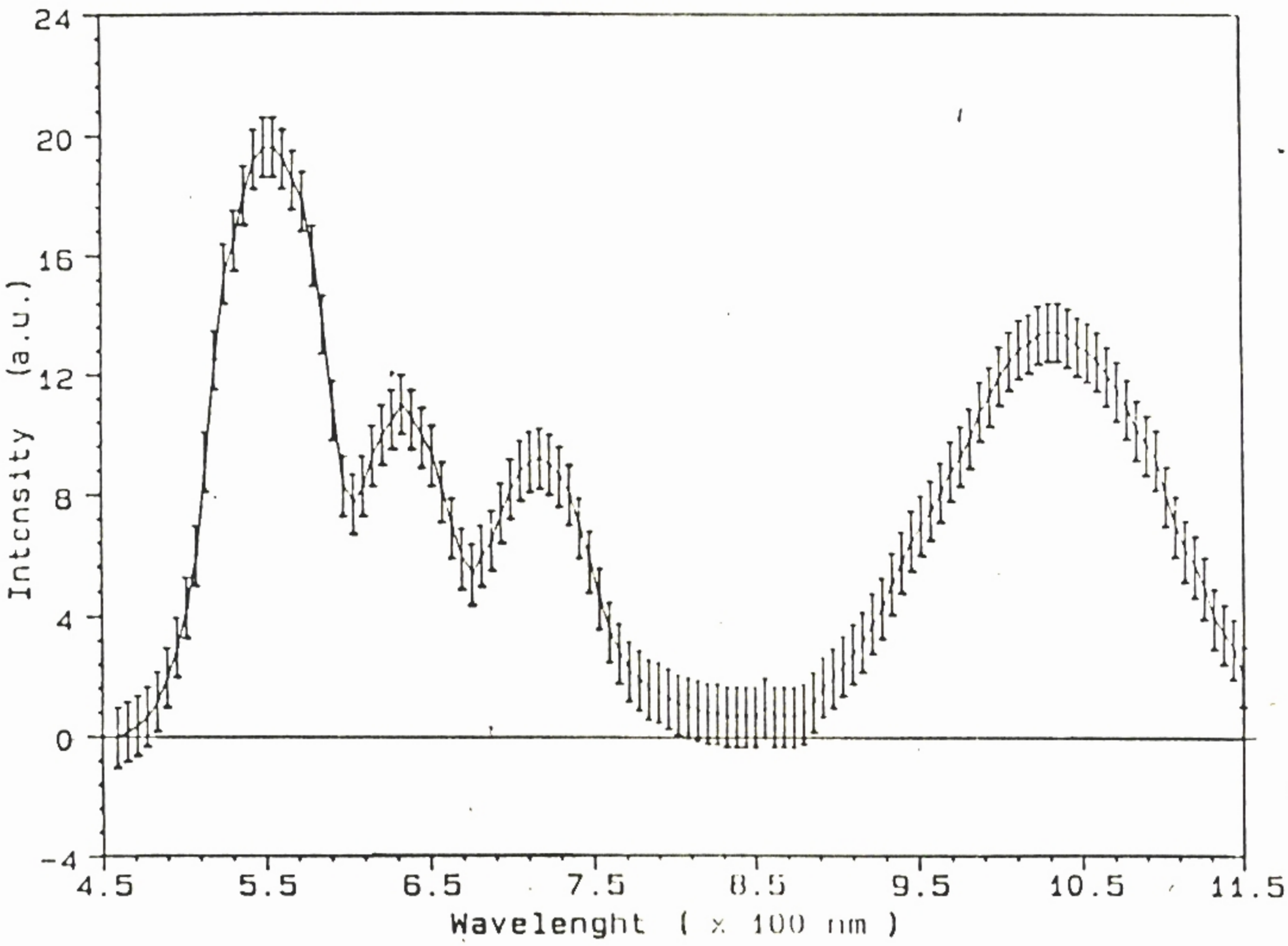

FIGURE 4. Excitation spectrum of a irradiated KCl:Tl crystal at 77K. Absorptions bands corresponding to the $Tl^{0}(1)$ centers peaking at 550, 720 and 1040 nm. The band centered at 635 nm was associated to the $Tl_2^{0}(1)$ centers.

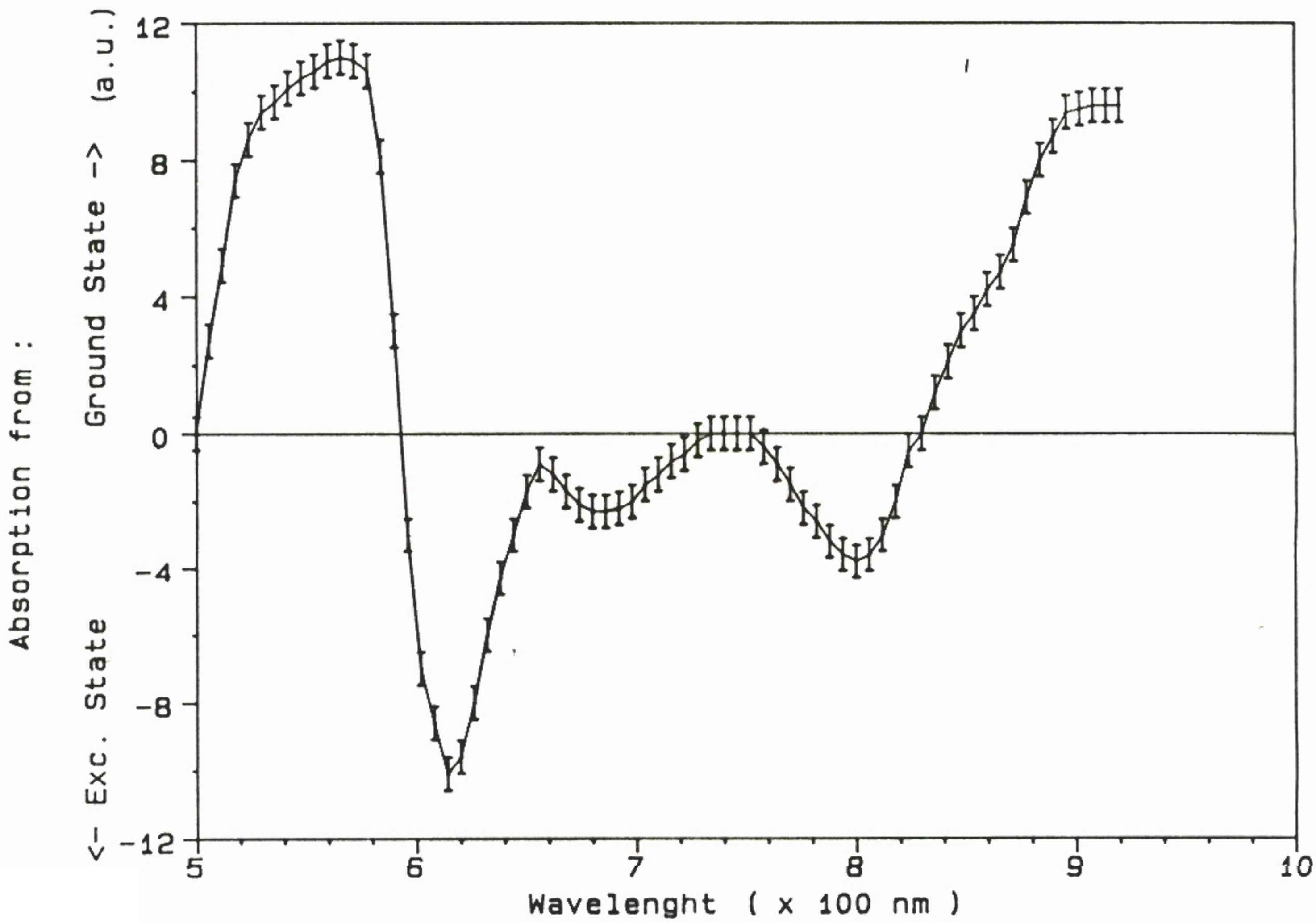

FIGURE 5. Results of the tagged absorption measurement on the KCl: Tl with the presence of defects associated to the Tl sample.

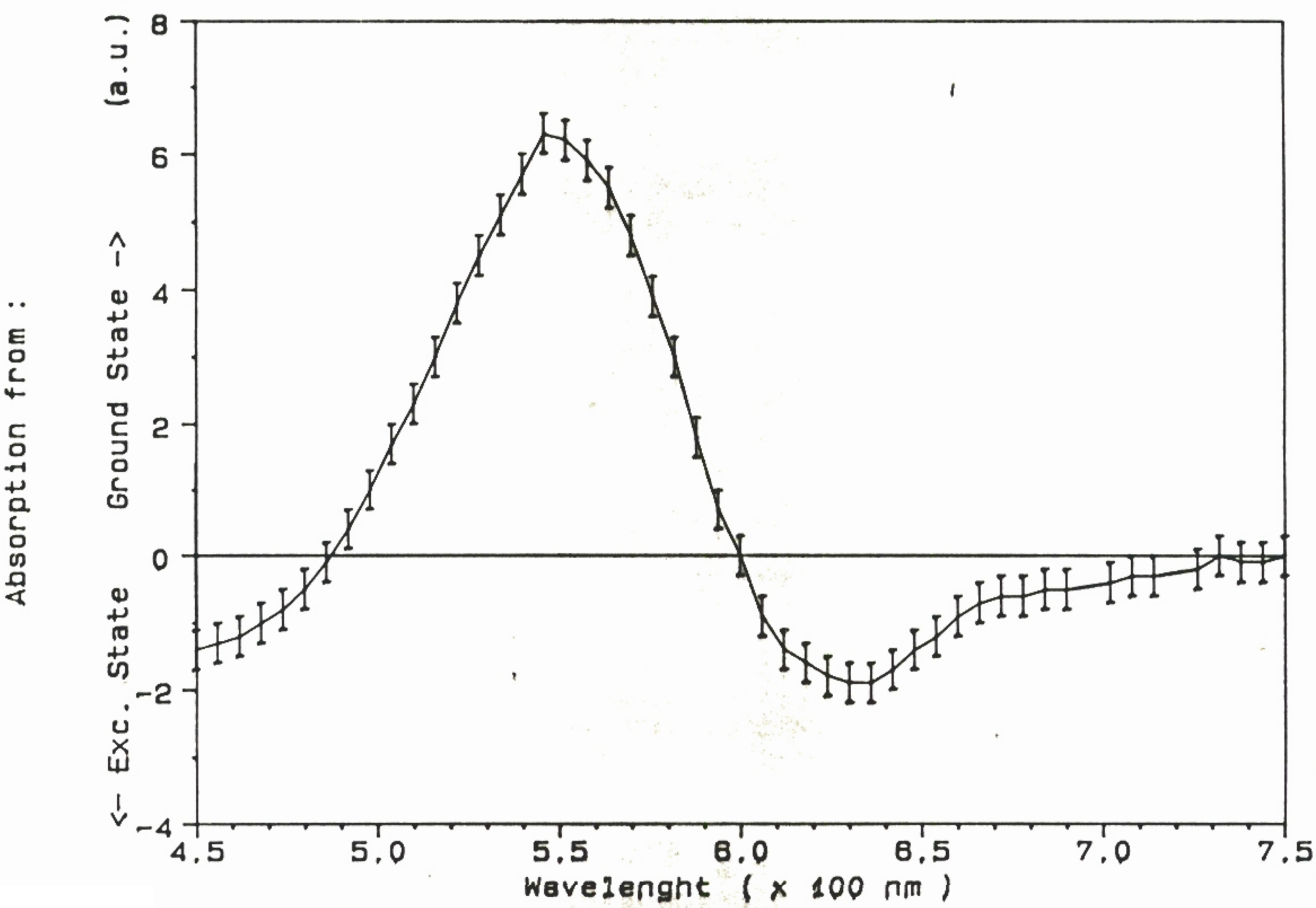

FIGURE 6. Results of the tagged absorption measurement on the $Tl^{0}(1)$ center in annealed samples before electron irradiation.