Solid State Communications, Vol. 50, No. 12, pp. 1037-1041, 1984.
Printed in Great Britain.

0038-1098/84 $3.00 + .00
Pergamon Press Ltd.

OPTICAL PROPERTIES OF THE $In^0(1)$ CENTER IN KCl

N. D. Vieira*, L. F. Mollenauer and L. H. Szeto

Bell Telephone Laboratories

Holmdel, NJ 07733 - Rm. 4C-306

(Received 5 December 1983 by A. G. Chynoweth)

We report both experimental and theoretical studies of the optical properties in KCl of a defect-associated In center whose sole previously identified optical transition was a strong absorption band peaking at 610 nm. With the aid of an optical tagging technique, we have been able to identify with that center two new but much weaker absorption bands peaking at 860 and 960 nm, respectively. We show that the energy splittings, relative strengths, and less perfectly, the polarizations of those three transitions make fit to the $In^0(1)$ center model, i.e., the model, initially developed for the $Tl^0(1)$ center, of a neutral atom perturbed by the field of an adjacent anion vacancy. However, in contrast to the $Tl^0(1)$ center, the $In^0(1)$ center lacks a significant emission, excluding its use as a laser gain medium.

Color centers in the alkali halides involving Tl, In and Ga impurity atoms associated with one or more anion vacancies were first discovered and analyzed by means of electron spin resonance[1,2,3]. More recent studies[4,5] of one of these, the $Tl^0(1)$ center, have served to identify its lower-lying optical transitions, and have shown a remarkable fit of the measured transition energies, oscillator strengths and the polarization character of the transitions to a model based on a (neutral) Tl atom perturbed by an essentially empty, nearest neighbor anion vacancy. In this paper we report similar optical studies of In doped KCl crystals. In particular, we have discovered a set of absorption bands whose behavior fits that to be expected of the analogous $In^0(1)$ center. However, quite unlike the laser-active $Tl^0(1)$ center[6,7], we find no emission definitely associated with the $In^0(1)$ center, and in fact, no *strong* emission of whatever origin in the In doped crystals.

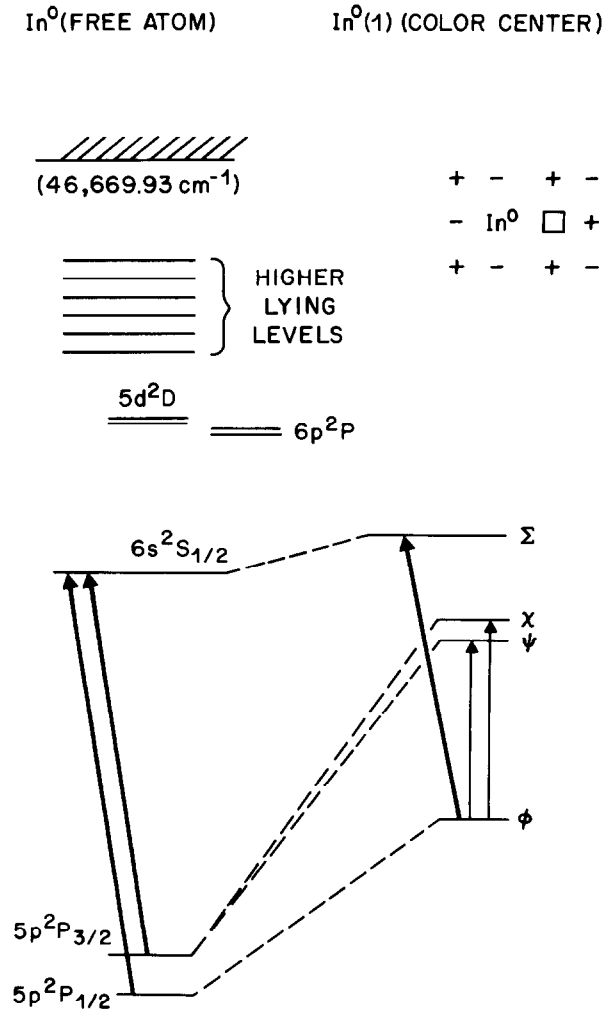
The simple crystal field model we use here (first described in Ref. 2) and its implications for the optical regime has been extensively detailed in Ref. 4. Therefore here we shall, in general, give only a brief qualitative sketch of that model, except when quantitative differences between the $Tl^0(1)$ and $In^0(1)$ centers dictate otherwise.

The electronic configuration of the In atom is [Kr] $4d^{10}5s^25p^1$, and we shall consider, as in the Tl case, that in effect one has to deal with a single electron. The atomic ground- and first-excited states are $^2P_{1/2}$ and $^2P_{3/2}$ respectively, separated by a spin orbit splitting of $\sim$2200 cm^{-1} (see Fig. 1). Both levels have a strong dipole transition to a $^2S_{1/2}$ state lying $\sim$24400 cm^{-1} higher in energy[8].

In the color center the adjacent anion vacancy provides an odd field that has even and odd parity terms. The even parity term of the field acts upon the free atom's $5p$ states, splitting them into 3 Kramer's doublets, $\phi^{\pm}$, $\psi^{\pm}$, and $\chi^{\pm}$ (see Fig. 1); it also mixes one component of the $5d$ orbital (the cubic component d_{z^2}) into the $6s$ state, generating the $\Sigma^{\pm}$ state. The odd parity term then mixes significant amounts of the Σ state into the $5p$-derived manifold (ϕ, ψ, χ), thus inducing transitions of modest oscillator strength within that manifold. These transitions can be well accounted for by the contribution of only the Σ state to the ϕ, ψ and χ states because of the large oscillator strengths connecting those states to the $6s$ and $5d$ states.[8]

As in Ref. 4, the state energies of the $5p$ manifold can be expressed (see Fig. 2) as a function of the ratio γ/Δ, where γ is a crystal field (energy) matrix element (for a precise definition of γ, see Ref. 4), and Δ is the effective spin orbit splitting of the In atom in the crystal. Also, as in Ref. 4, one can then make a fit of the measured $\phi \rightarrow \psi$ and $\phi \rightarrow \chi$ transition energies to the calculated splittings. Anticipating those

* Visiting scholar from Instituto de Pesquisas Energeticas e Nucleares, São Paulo, Brazil, under a fellowship from Brazilian Nuclear Energy Commission (C.N.E.N.)



[1] Energy levels diagram of the In atom (left side) and of the $In^0(1)$ color center. The states labeled ϕ, ψ and χ have a large $5p$ character, while the Σ state is derived largely from the atomic $6s$ state. The ϕ and ψ states contain significant admixture of the Σ state.

experimental results, we find a best fit for $In^0(1)$) of $\gamma/\Delta = 1.87$. From that ratio we can then immediately (again, as in Ref. 4) write down wavefunctions with specific coefficients. Furthermore, the measured $\phi \rightarrow \Sigma$ and $\psi \rightarrow \Sigma$ transition energies allow for computation of the relative coefficients of admixture of the Σ state in the other two states. The wavefunctions then become:

$$|\phi^{\pm}\rangle = 0.996\, R_p|10\rangle^{\pm} - 0.088\, R_p\,|\,1\pm1\rangle^{\mp} + \beta\, R_s|\Sigma^{\pm}\rangle$$

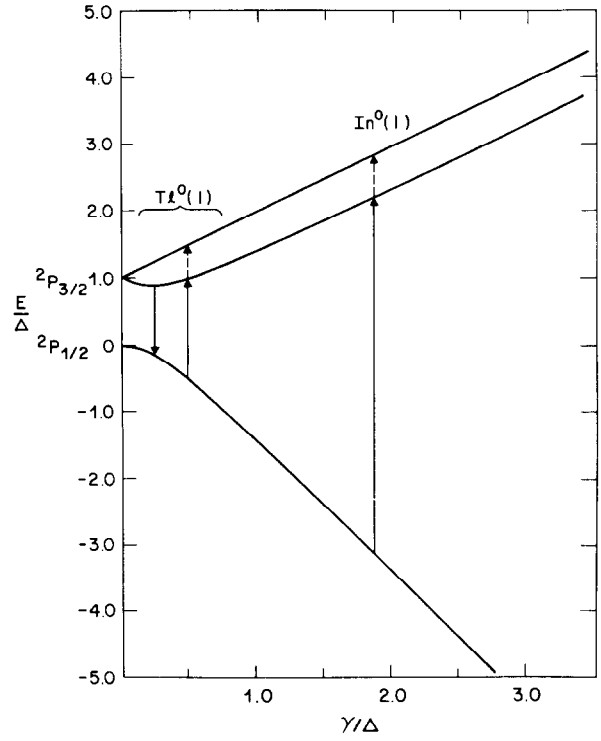
$$|\psi^{\pm}\rangle = 0.088\, R_p|10\rangle^{\pm} + 0.996\, R_p\,|1\pm1\rangle^{\mp} + \beta/4\, R_s|\Sigma^{\pm}\rangle$$

$$|\chi^{\pm}\rangle = R_p|\,1\pm1\rangle^{\pm}$$

$$|\Sigma^{\pm}\rangle = \cos\theta\, R_s|\,\infty\rangle^{\pm} + \sin\theta\, R_s\,|\,20\rangle^{\pm} \qquad (1)$$

where the superscript $\pm$ refers to the m_s component of the spinorial part of the wavefunctions ($+\frac{1}{2}$,$-\frac{1}{2}$), R_p and R_s are the radial wave functions, and where β and θ are parameters to be determined by fit to experiment.[9]

The $In^0(1)$ centers in KCl were obtained in a similar way to that used for the $Tl^0(1)$ centers.[4] Crystals of KCl doped with ~0.1 mol % In were irradiated (crystal temperature ~−100 °C) by an electron beam and then at higher temperatures were illuminated with white light for ~15 min. The optimal



[2] Energies of the 5*p* manifold as a function of the crystal field strength parameter, γ. Both quantities are normalized by the spin orbit splitting.

temperature for the latter process was ~20°C, a value considerably higher than the optimum (-30°C) for the $Tl^0(1)$ center formation; this higher temperature apparently helps to minimize the formation of other In-associated centers (Ref. 3). We could also increase the rate of $In^0(1)$ center formation by using only blue-green light, consistent with the discovery[10] that illumination of the 610 nm band at high temperature reduces the $In^0(1)$ center density.

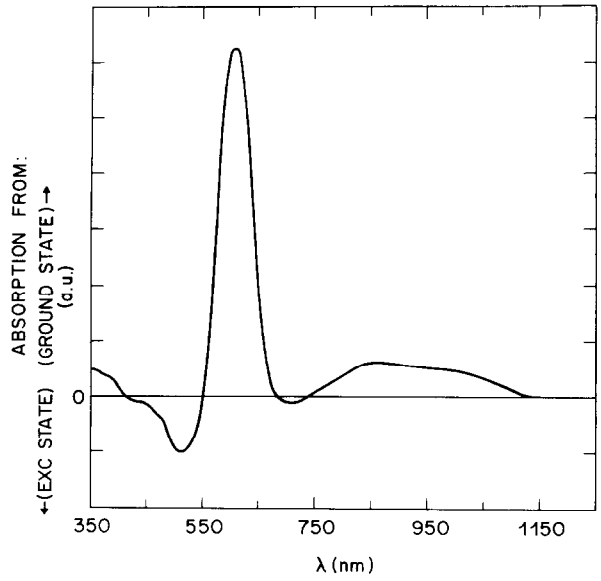
To determine the bands belonging to the $In^0(1)$ center, we used a tagging technique (Ref. 11) that involves pumping one of the known bands of the species under study with a chopped laser beam and probing of the pumped spot with a low intensity tunable beam. The resultant absorption signals are then electronically normalized and analyzed with a phase sensitive detector. The signals from ground and excited state absorption lag the pump beam modulation by phase angles of ϕ and $180° + \phi$, respectively. For less than saturated pumping, ϕ can be calculated as

$$\phi = \tan^{-1}(\omega\tau) \qquad (2)$$

where ω is the modulation frequency and τ is the decay time.

In particular, we used the 647 nm line of a Kr ion laser modulated at a frequency of 50 kHz to pump the $In^0(1)$ 610 nm band; the resultant modulated absorption signals are shown in Fig. 3. There are two overlapping ground state absorption bands in the infrared region, with peaks at ~860 nm and ~960 nm, respectively. The longer wavelength band has a certain overlap with the 1064 nm line of a Nd:YAG laser, and by pumping in this region we reconstructed entirely the visible part of the spectrum (Fig. 3 is actually a normalized composition of the two measurements.) The phase shifts obtained with either of the pump lines were always less than 4°, usually even smaller, less than 2°, implying a decay time considerably *less* than 200 nsec. (This relatively short decay time resulted in a considerably smaller population modulation, and hence correspondingly smaller signals than were obtainable (Ref. 4) with the $Tl^0(1)$ centers.

If we now associate the 960, 860 and 610 nm bands with the $\phi \rightarrow \psi$, $\phi \rightarrow \chi$ and $\phi \rightarrow \Sigma$ transitions, respectively, the corresponding energy splittings make a credible fit to the model. First, from the infrared band peaks, we can calculate the effective spin orbit splitting (Δ) and the crystal field energy parameter (γ), much as was done in Ref. 4. We obtain $\Delta = 1940\ cm^{-1}$, 12% smaller than in the free atom, and $\gamma = 3625\ cm^{-1}$. The fitting of the data is shown in Fig. 2, where for easy comparison the similar fitting for the $Tl^0(1)$ center



[3] Results of the tagged-absorption measurement on the $In^0(1)$ center. The graph is a normalized composition of the results obtained by pumping in the 610 and 960 nm bands.

made in Ref. 4 is also shown. Comparing these quantities with the ones obtained for the $Tl^0(1)$ center, we see that for the $Tl^0(1)$ case, the reduction in spin orbit splitting was larger (17%) and the crystal field energy (3250 cm^{-1}) was about 10% smaller. Considering the difference in atom sizes and nature of the wavefunctions, the crystal field energies are not expected to be any closer.[12]

In the modulated-pumping (tagging) experiment described before, we observed the following polarization characteristics of the transitions:

a) For pumping along a 100 axis with the 647 nm line, the 610 nm absorption is almost completely polarized parallel to the pump.

b) For pumping along a 100 axis with the 1064 nm line, the 610 nm absorption shows a polarization ratio of 0.8 ($\|/\perp$ with respect to the pump).

c) There was not a clear polarization of the infrared bands when the 610 nm band was pumped, i.e., polarization ratios could not be obtained due to the small amplitude of the signals.

In order to understand the polarization dependences and strengths of these transitions, we have to consider that in the $In^0(1)$ case, where the crystal field splitting is many times the effective spin orbit splitting, the character of the resulting wavefunctions tends to be relatively pure. That is to say, from expression (1) we see that the ground state is essentially a p_z orbital and the excited states are essentially p_{xy} type. Therefore, we can expect the transition from the ground state (ϕ) to the Σ level to be strongly allowed and to have a very strong polarization along the z axis of the center. This polarization is further enhanced by a constructive interference of the d_{z^2} part of the Σ wavefunction. In fact, we measured an essentially pure z-polarized transition, purer than for the $Tl^0(1)$ center, where the ground state has not such a strong p_z orbital character and the interference effects are not as large.

The admixture of Σ state into the various wavefunctions of the $5p$ derived manifold depends on the amount of p_z orbital in the particular wavefunctions. Thus, according to expression (1), the ground state has four times more admixture of Σ state than the ψ state and the χ state has none. In view of this preponderance of the Σ state admixture into the ground state, at first, one would think that the character of the $\phi \rightarrow \psi$ and $\phi \rightarrow \chi$ transitions is mostly determined by the p orbital character of the ψ and χ wavefunctions, respectively. Considering the pure or nearly pure p_{xy} character of the ψ and χ wavefunctions (again, see expression (1)), one would then expect the major contribution to the transitions cross sections to be:

$$\sigma_{xy} \propto |\langle p_{xy} | x \pm iy | \Sigma \rangle|^2 \qquad (3)$$

However, the experimentally determined polarization ratios of the $\phi \rightarrow \psi$ and $\psi \rightarrow \phi$ transitions are more nearly unity, as described above. Detailed calculations have shown that for a particular s and d_{z^2}

composition of the Σ state, interference effects in the transition matrix elements can account for a greatly reduced size of σ_{xy} for both of the transitions in question. (The corresponding value of θ (see Eq. (1)) is 33°, as opposed to the smaller value of 18° obtained for the $Tl^0(1)$ center; the larger value of θ is consistent with the purer polarization character of the $\phi \rightarrow \Sigma$ band for $In^0(1)$ as opposed to Tl^0 (1).) Thus it is possible to explain both the greatly reduced strength of the infrared transitions of the $In^0(1)$ center with respect to that observed for the $Tl^0(1)$ center, as well as the observed polarization ratios, mentioned above, of the $\phi \rightarrow \psi$ transition. However, the presence of a nonzero z polarization component in the $\phi \rightarrow \chi$ transition must be due to small contributions of other admixed states that are not considered in our simple model.

Although we searched for the $In^0(1)$ center emission at temperatures as low as 4K, and in spite of the fact that we used strong laser sources for excitation, we could not find any emission definitely associated with that center. (The search was carried out to the limit set by the quartz dewar windows, $\lambda \lesssim 3.5\ \mu m$). Considering that fact and the short lifetimes implied by our modulated absorption measurements, we conclude that return to the ground state is dominated by strong nonradiative transitions. The origin of these nonradiative transitions is simply unknown. Perhaps it has to do with a tendency for impurity ions (stronger for In than for Tl) to form many other species, some of which may couple strongly to the potential $In^0(1)$ emission.

In conclusion, we have discovered two new absorption bands (bands different from the one band known previously[9]) associated with the $In^0(1)$ center, and we have shown that the energy splittings, relative probabilities and polarization of all three transitions generally make a rather good fit to the simple crystal field model that has been so successful with the $Tl^0(1)$ center. However, the lack of an associated emission for the $In^0(1)$ center (in stark contrast to the behavior of the $Tl^0(1)$ center) remains a complete mystery.

REFERENCES

[1] P. G. Baranov and V. A. Khramtsov, "EPR Study of Impurity Colour Centres in P-state in Alkali Halides," Phys. Stat. Sol. (b) **101**,153 (1980).

[2] E. Goovaerts, J. Andriessen, S. V. Nistor and D. Schoemaker, "Electron-spin Resonance Stufy of Tl Atom Defects in KCl and Relativistic Many-Body Analysis of the Hyperfine Structure," Phys. Rev. B, **24**,29 (1981).

[3] Willy Van Puymbroeck, Johannes Andriessen and Dick Schoemaker, "Complex Ga^0 ($4p^1$) and In^0 ($5p^1$) Centers in KCl. Electron Spin Resonance Study," Phys. Rev. B, **24**, 2412 (1981).

[4] L. F. Mollenauer, N. D. Vieira, and L. S. Szeto, "Optical Properties of the $Tl^0(1)$ Center in KCl, Phys. Rev. B, **27**, 5332 (1983).

[5] F. J. Ahlers, F. Lohse, J. M. Spaeth and L. F. Mollenauer, "Magneto-Optical Studies of Atomic Thallium Centers in KCl: Magnetic Circular Dichroism Tagged by Spin Resonance," Phys. Rev. B, **28**, 1 (1983).

[6] W. Gellerman, F. Luty and C. R. Pollock, "Optical Properties and Stable, Broadly Tunable cw Laser Operation of New F_A-type Centers in Tl^+-Doped Alkali Halides," Optics Comm. **39**, 391 (1981).

[7] L. F. Mollenauer, N. D. Vieira and L. Szeto, "Mode Locking by Synchronous Pumping Using a Gain Medium with Microsecond Decay Times," Optics Letters, **7**, 414 (1982).

[8] N. P. Penkin and L. N. Shabamova, "Oscillator Strengths and Effective Cross Sections of the Resonance Lines of Gallium and Indium Atoms for Line-Broadening Collision," Optics Spectrosc. **23**, 11 (1967)

[9] Note that we do not distinguish between the $5p_{1/2}$ and $5p_{3/2}$ radial wavefunctions; this non-relativistic approximation has little effect on the quantities to be calculated here. In like manner, for simplicity, the radial part of the $5d$ wavefunction has been taken equal to -1 times the radial part of the $6s$ state; this approximation is justified by a comparison with known analogous Tl wavefunctions.

[10] P. G. Baranov and V. A. Khromtsov "Electron Spin Resonance of Indium and Gallium Centers in Alkali Halide Crystals," Sov. Phys. Solid State, **21** (5) (1979).

[11] L. F. Mollenauer "Excited State Absorption Spectrum of F_2^+ Centers and the H_2^+ Molecular Ion Model," Phys. Rev. Lett., **43**, 1524 (1979)

[12] We note that multiplying the $Tl^0(1)$ γ/Δ ratio (0.50) by the ratio of the free atom's spin orbit splitting yields $\gamma/\Delta = 1.77$ for $In^0(1)$, a value only 5% less than the value obtained from the best fit to the experimental data.