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The nature of the x-ray-induced luminescence and the hole centres in CsI:Tl studied by optically detected electron paramagnetic resonance

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Abstract. In the x-ray-induced luminescence band peaking at 560 nm we have detected the electron paramagnetic resonance (EPR) spectrum using optical detection (ODEPR) of V_K centres, which have their molecular axes perpendicular to the magnetic field. An EPR was only detected as a microwave-induced change in the magnetic circular polarization of the emission, and not as an emission intensity change. No parallel centres were seen, nor any trapped electron centre. The observations are explained as a recombination luminescence of a kind of Tl-bound exciton. Furthermore, the ODEPR via the magnetic circular dichroism of the absorption of V_{KA} centres generated by x-irradiation at 4.2 K and trapped near Tl^+ and near Na^+ were measured. These centres are room-temperature stable for a few minutes and responsible for afterglow effects when using CsI:Tl, Na as x-ray-scintillator crystals.

1. Introduction

The CsI crystal doped with Tl^+ is one of the best known and most used x-ray-scintillator crystals. The x-ray-induced luminescence band (henceforth simply called the x-ray luminescence band) extends from 300 to 800 nm in the visible spectral region with a peak at about 560 nm at room temperature (Fowler 1969). At low temperature the luminescence band is somewhat structured and may be composed of two to three bands (Holzapfel 1983). Although the x-ray luminescence band, which is also excited as a photo-luminescence band, was studied intensively for a long time, there is a controversial discussion about the nature of this luminescence band. It was interpreted as being a Tl^+ intra-centre transition (Masunaga *et al* 1966, Fowler 1969), as a donor–acceptor recombination between a Tl^0 atom and a hole centre (Gutan *et al* 1974), which was thought to be a V_K centre (a hole shared between two adjacent halogen ions), and also as due to a recombination luminescence of an exciton captured at a Tl^+ ion (Smol'skaya and Koleszikova 1979). If the donor and a hole are involved in a recombination luminescence, then these paramagnetic centres should be detectable in an electron paramagnetic resonance (EPR) experiment using optical detection via the luminescence band (see e.g. Spaeth *et al* 1992). No such experiments, however, have been reported to date.

When applying CsI:Tl crystals as x-ray detectors and rapidly scanning the x-irradiation, as is done in computer tomography, one disadvantageous feature of those scintillators is the existence of an afterglow luminescence. The reasons for the afterglow luminescence are not yet understood. It was shown that the additional doping of alkaline-earth ions does

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not influence the luminescence properties and that doping with other ions usually improved the afterglow properties only at the expense of a diminished luminescence yield (Langhans 1985, Lindner 1987). Thermoluminescence studies revealed the importance of V_K centres as mobile hole traps, which upon recombination showed luminescence at 560 nm (Holzapfel 1983). Thus it could be speculated that V_K centres as radiation damage defects, possibly stabilized at impurities, play an essential role in the afterglow effects.

It is the purpose of this paper to report on magneto-optical and optically detected EPR (ODEPR) experiments on x-irradiated CsI:Tl. The nature of the x-ray luminescence was investigated with EPR detected in the x-ray luminescence and the participation of a hole centre in the luminescence process could be established. Furthermore, the existence of short-lived V_K centres stabilized at the activator Tl^+ could be evidenced using EPR detected via the magnetic circular dichroism of the absorption (MCDA). It is thus shown that afterglow effects cannot be avoided in CsI:Tl.

2. Experiment

The CsI crystal was doped with 1 mol% Tl^+ in the melt and provided by Ch Grabmaier (Siemens AG, München). The luminescence was excited either by x-rays (70 kV, 15 mA) *in situ* perpendicularly to the optical axis of the spectrometer or by the unfiltered light of a deuterium lamp. The detector, a photomultiplier, was protected by a 400 nm edge filter. The custom-built computer-controlled spectrometer to measure EPR with optical detection allowed us to measure ODEPR either via the MCDA or via the magnetic circular polarization of the emission (MCPE) in the K band (24 GHz). The spectrometer could be operated between 220 nm and 1700 nm and between 1.5 K and 300 K. For details of the set-up see e.g. the book by Spaeth *et al* (1992).

3. Experimental results

3.1. ODEPR via x-ray luminescence

When trying to measure the ODEPR signal as a microwave-induced intensity change in the x-ray luminescence or in the UV-excited photoluminescence in the 560 nm band, no signals could be observed. Thus, the speculation that the luminescence might be due to a Tl^0 (donor)–V_K centre (acceptor) recombination in analogy to what was often found in semiconductor crystals between shallow donors and acceptors ($D^0 + A^0 \rightarrow D^+ + A^-$) could not be confirmed. With this statement we refer to the common observation that there is a bottleneck for the donor–acceptor-pair recombination luminescence, which is changed by the spin flips and results in a luminescence intensity change upon inducing EPR transitions. The case where there is no bottleneck will be discussed later. Had the emission contained the radiative decay of a triplet state such as expected from triplet excitons trapped at a Tl^+, then we should have expected a signal in this detection scheme, similarly to what was found for the self-trapped exciton in AgCl, for example (see e.g. Song and Williams 1993). The same negative result was obtained for photo-excitation with the deuterium lamp.

However, a signal could be measured when detecting the MCPE instead of the intensity change. Figure 1, trace a, shows the spectrum obtained. An EPR line with $g = (2.26 \pm 0.01)$ and a half width of $\Delta B_{1/2} = (56 \pm 2)$ mT was measured in the x-ray luminescence. The emission was detected between 400 and 800 nm. The g-factor is identical within experimental error to that found with conventional EPR for V_K centres in CsI that have

their axes perpendicular to the static magnetic field, henceforth called perpendicular centres (Pilloud and Jaccard 1975). As will be explained in detail in the next section, figure 1, trace b, shows the MCDA-detected EPR spectrum for perpendicular V_K centres created at 4.2 K by x-irradiation. The two spectra (halfwidth, g-factor) are identical within experimental error ($\Delta B_{1/2}$ = (54±2) mT). The slight shift in the field position is due to the slightly different microwave frequencies used in the two experiments. Thus, in the MCPE (and not in the intensity change) the EPR spectrum of perpendicular V_K centres is detected proving that in the x-ray luminescence of CsI:Tl^+ a hole centre plays an important role. No evidence was found for an electron-trap centre in the ODEPR spectrum.

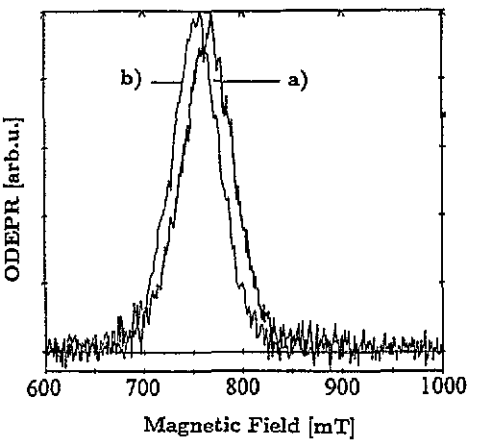

Figure 1. Trace a, the ODEPR spectrum measured at 1.6 K via the MCPE of the x-ray-induced luminescence of CsI:Tl (microwave frequency 24.047 GHz). B_0 ||[001]. Trace b, the ODEPR spectrum of V_K centres is CsI:Tl measured at 1.6 K via the MCDA at 2.04 eV for B_0 ||[001] (microwave frequency 23.935 GHz).

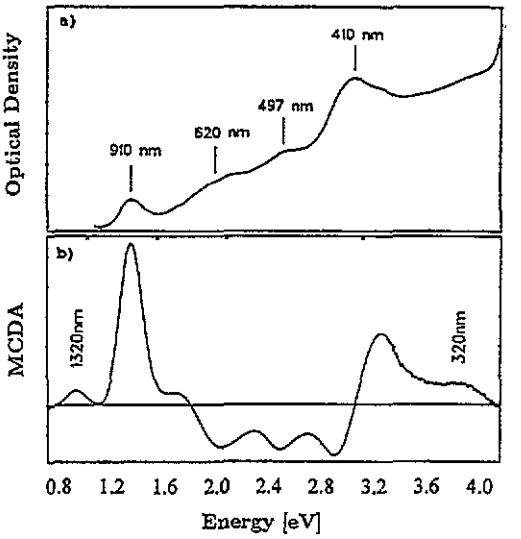

Figure 2. The absorption and MCDA spectra of CsI:Tl (doping level 1 mol% in the melt) after x-ray-irradiation for 30 min at 4.2 K. (a) Absorption at T = 1.6 K; (b) MCDA at T = 1.6+K, B_0 = 3 T.

After switching off the x-ray excitation a long afterglow emission is observed, which is the same Tl-related band at 560 nm. This afterglow can be seen for hours at 1.5 K. Also in this afterglow emission the MCPE-detected EPR spectrum of perpendicular V_K centres is observed. The afterglow is thought to be due to a tunnelling recombination of trapped electrons with the V_K centres.

3.2. ODEPR via MCDA in x-irradiated CsI:Tl

Figure 2(a) shows the optical absorption bands generated by x-irradiation of CsI:Tl at 4.2 K in the spectral range between 0.8 and 4.0 eV. Above 4 eV the optical density is very high due to the Tl^+-related absorption bands (note that the doping level was as high as 1 mol% in the melt). Figure 2(b) shows the corresponding MCDA spectrum. The intensities of all the MCDA bands measured are temperature dependent, thus they all belong to paramagnetic centres (see e.g. Spaeth *et al* 1992). The three bands at 3 eV (410 nm), 2.5 eV (497 nm) and 2.0 eV (620 nm) were described previously. The band at 3 eV was assigned to the

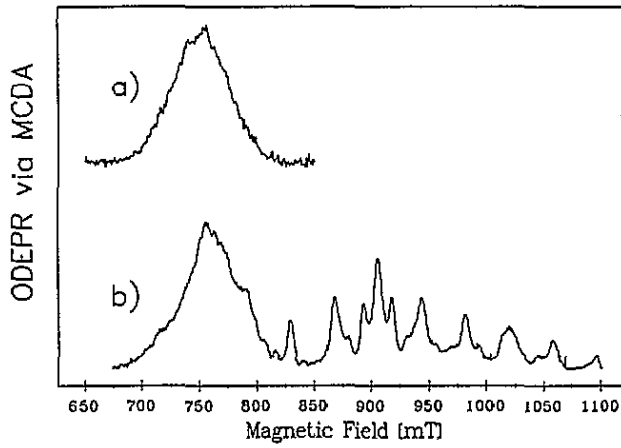

Figure 3. (a) The ODEPR spectrum of CsI:Tl, x-irradiated at 4.2 K *in situ*, measured at 1.5 K via the MCDA at 2.04 eV (microwave frequency 23.94 GHz); B_0 ||[100]; (b) the same measured at 0.94 eV.

$^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transitions of V_K centres (Sidler *et al* 1973). The bands at 0.94 eV (1320 nm) and 1.36 eV (910 nm) have not been previously reported.

Figure 3(a) shows the ODEPR spectrum recorded at 2.04 eV for B_0 ||[100]. This line is also measured when recording ODEPR in the MCDA bands at 2.88 eV and 1.72 eV. When measuring in the MCDA band at 0.94 eV, the spectrum of figure 3(b) is measured. It contains a similar broad line at 750 mT and additional lines at higher fields. The peak of the lines at 750 mT corresponds to $g = (2.27 \pm 0.02)$ and agrees with that of perpendicular V_K centres (Pilloud and Jaccard 1975). The half-width is 60 mT; the line shows indications of a hyperfine (HF) structure. The g-factor of the parallel V_K centres (i.e. of those with their molecular axis parallel to the static magnetic field), $g_\parallel = 1.89$ (Pilloud and Jaccard 1975), corresponds to the field of 905 mT where the strongest line is found in the high-field region. Since the nuclear spin of ^{127}I is $\frac{5}{2}$ for two equivalent nuclei, an 11-line HF pattern with an intensity ratio of 1:2:3:4:5:6:5:4:3:2:1 is expected. Eight HF lines with the expected HF separation of 36 mT are seen in figure 3(b) (three lines are superimposed by the spectrum of the perpendicular centres). However, in addition there are a number of satellite lines, most clearly seen around the line at 905 mT. It looks as if the V_K centres created are 'perturbed' by being trapped at an impurity as a V_{KA} centre. In order to test whether the additional splitting is caused by an HF interaction with Tl (there are two isotopes ^{203}Tl with 29.5% abundance and ^{205}Tl with 70.5% abundance, both having $I = \frac{1}{2}$) we have performed an analogous experiment in Na-doped CsI (doping 1 mol% in the melt). Figure 4 shows the EPR spectra measured at 0.94 eV for both the Na- and Tl-doped CsI crystals for B_0 ||[100]. As can be seen, the satellite splitting structure is very similar in both cases. Since the nuclear spin of ^{23}Na is $\frac{3}{2}$ (100% abundance) and since the nuclear moments of Tl and Na differ considerably (that of ^{23}Na is about half that of the Tl isotopes) it can be ruled out that the satellite splitting is caused by HF interaction with Na^+ or Tl^+ impurities. The perturbation must have another explanation.

The EPR lines can be measured in all the MCDA bands as was shown by measuring the MCDA tagged by EPR (figure 5), a kind of excitation spectrum of the ODEPR lines (for details see e.g. Spaeth *et al* 1992). In this tagging experiment, we cannot distinguish between the perpendicular centres of 'perturbed' (see below) and unperturbed V_K centres.

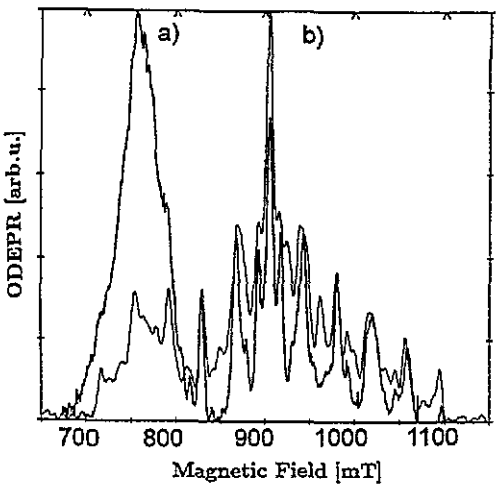

Figure 4. The ODEPR spectrum measured via the MCDA at 0.94 eV in CsI:Tl (trace a) and CsI:Na (trace b). Both crystals were x-irradiated at 4.2 K *in situ* for 30 min; T = 1.5 K; B_0 ||[100].

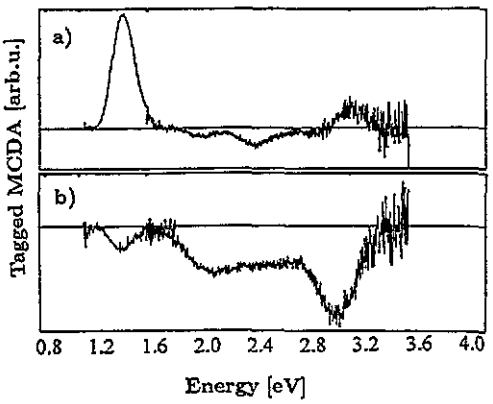

Figure 5. Tagged MCDA spectra of CsI:Tl x-irradiated at 4.2 K *in situ* measured at 1.6 K, microwave frequency 23.94 GHz, B_0 || [100]: (a) exciting the EPR at 750 mT (perpendicular V_{KA} centres); (b) exciting the EPR at 905 mT (parallel V_{KA} centres).

Not shown in figure 5 is that the line at 0.94 eV is also an optical transition of these perturbed V_K centres. Note that the EPR lines measured at 3 eV and at 1.36 eV have opposite signs. Above 3.3 eV the signal-to-noise ratio was too low to measure the tagged MCDA.

Upon warming to room temperature, the perturbed V_K centres disappear within a few minutes. Thus, their stability is higher than that of unperturbed V_K centres, a fact generally known for V_{KA} centres (see e.g. Fowler 1969).

4. Discussion

4.1. X-ray luminescence

The problem here is to explain why we observe perpendicular V_K centres but not parallel ones and why we do not see the electron centre that upon recombination with the hole centre gives rise to the Tl-related emission band. We also need to discuss why the MCPE signal of the V_K centres is so weak compared to the strong luminescence signal. As mentioned in subsection 3.1 we have not seen the ODEPR as a luminescence intensity change, but only in the MCPE. For a donor–acceptor-recombination luminescence no luminescence intensity change but only a change in the MCPE is observed upon EPR transitions, if donors and acceptors are thermalized before recombining. Then there is no bottleneck for the recombination luminescence. In this case, however, all centre orientations should have been observed, i.e. in our geometry also the parallel centres. Therefore, we cannot explain our observations with a model in which we have a Tl^0 (donor)–V_K centre (acceptor) recombination luminescence in analogy to what is discussed in semiconductor physics between shallow donors and acceptors.

As to magneto-optical properties of V_K centres in KBr, recently their MCDA was studied in detail (Spaeth *et al* 1994). It turned out that the usual simple model of a molecular ion X_2^-, which consists of a linear combination of two hole valence p orbitals along [110] in

D_{2h} symmetry, is not sufficient to explain the observations. According to this model the UV absorption band is a $^2B_{1u} \rightarrow {}^2A_g$ transition and the two IR bands due to the dipole-allowed transitions from $^2B_{1u}$ to the spin–orbit-split $^2B_{3g}$ and $^2B_{2g}$ states. However, a calculation of the matrix elements for circularly polarized transitions showed that no MCDA is to be expected for V_K centres that have their axes parallel to the magnetic field. There are MCDA transitions for centres with their axis perpendicular to the magnetic field both in the UV and in the IR transitions due to the effect of spin–orbit and magnetic-field mixing of the states for this field orientation. This was indeed found experimentally: one does observe UV and IR MCDA bands, but the MCDA-detected EPR is only observed for perpendicular centres and of those with other orientations except for parallel centres. The intensity of centres with e.g. 45° is already very weak (Spaeth *et al* 1994).

The starting elements for our analysis of the emission are the following.

(i) In the case of MCPE (a hole with a Tl nearby and an excited electron), we think that the symmetry (D_{2h}) is conserved. However, in the case of MCDA of Tl-associated V_K centres, where there is no electron present, the symmetry of the V_K centre is lowered by the presence of the Tl^+ (see subsection 4.2). It is speculated that this difference may be due to the excited electron, which forms a kind of Tl-associated self-trapped exciton (STE), which pushes away the V_K core. In the perfect crystal in the STE there is an off-centre split of the hole and the electron in many cases (see e.g. Song and Williams 1993).

(ii) The excited electron, which is somewhat away from the V_K centre, is not coupled strongly to the hole spin, such that we consider the system as that of two non-interacting doublets. The electron wave function is assumed to be s like, e.g. 7s of Tl^0.

The Tl^0 6p orbital is occupied in free atoms; however, in the solid the levels often change and it is possible that we have an s-like one here. The s-like electron wave function ϕ_e is expanded about the centre of the V_K centre in terms of the molecular orbitals (MOs) and, in principle, their higher excited states. Whether the electron is in an s-like or p-like orbital does not matter for our arguments as long as the orbitals are diffuse. We only have to pick the s-like component from the expansion. In the case of a p-like orbital we would have to consider in principle a spin–orbit coupling, which may, however, be neglected if the p orbital is diffuse, which it certainly will be. We consider explicitly two geometries: the V_K centre axis parallel and perpendicular to the static magnetic field. The local coordinate system of the V_K centre, x, y, z (z being the molecular axis), and the laboratory system, X, Y, Z, are identical.

(a) $V_K \parallel B \parallel k \parallel z$. The luminescence is essentially that of the return of $\phi_e(r'; \alpha)$ to $|\Sigma_u; \alpha\rangle$. $\phi_e(r')$ is expanded as

$$\phi_e(r'; \alpha) = \sum a_i |i; \alpha\rangle = a_1|\sigma_g; \alpha\rangle + a_2|\pi_g; \alpha\rangle + a_3|\pi_g; \alpha\rangle + \ldots$$
$$= a_1|s; \alpha\rangle + a_2|xz; \alpha\rangle + a_3|yz; \alpha\rangle + \ldots \quad (1)$$

(the hole state being of odd parity (u), we consider only the even-parity (g) electron state for the dipole transition). The a_i are coefficients of expansion and a_1 may be assumed to be the largest. (Any function can be expanded about an arbitrary point using Legendre polynomials, see e.g. Song and Williams 1993, p 57.)

Each of the above molecular orbitals can be expanded to account for the mixing through the magnetic field B and spin–orbit coupling, as was shown by Fowler *et al* (1973). Here we can neglect the spin–orbit-coupling mixing because the above ϕ_e state is s like.

$|\Sigma_u; \alpha\rangle$ is expanded as

$$|\Sigma_u; \alpha\rangle = |z; \alpha\rangle + A_1|x; \beta\rangle + A_2|y; \beta\rangle. \quad (2)$$

Hereafter, the A represent spin–orbit mixing, and are obtained from perturbation theory. They contain the spin-orbit-coupling parameter of the halogen atom and the energy difference between the mixing MOs.

The dipole matrix of interest is, after neglecting terms of wrong spin

$$a_1\langle z;\ \alpha|x \pm \mathrm{i}y|s;\ \alpha\rangle + a_2\langle z;\ \alpha|\ldots|xz;\ \alpha\rangle + a_3 z;\ \alpha|\ldots|yz;\ \alpha\rangle$$
$$= a_2\langle z;\ \alpha|x|zx;\ \alpha\rangle \pm \mathrm{i}a_3\langle z;\ \alpha|y|yz;\ \alpha\rangle \neq 0. \tag{3}$$

However, the left and right circularly polarized signals cancel, because the two dipole moments are complex conjugates of each other: $I_+ - I_- = 0$.

In this order of approximation, therefore, there is no MCPE in this geometry.

(b) $V_K \perp \boldsymbol{B} \parallel \boldsymbol{k} \parallel x$. $\boldsymbol{B}$ and $\boldsymbol{k}$ are parallel to x, and the MCD dipole is $(y \pm \mathrm{i}z)$. $\phi_e(r';\ \alpha)$ is expanded as in (a) above, but $|\Sigma_u;\ \alpha\rangle$ is expanded differently:

$$|\Sigma_u;\ \alpha\rangle = |z;\ \alpha\rangle - \mathrm{i}|z;\ \beta\rangle + A_1|x;\ \beta\rangle + A_2|y;\ \beta\rangle + B_1|y;\ \alpha\rangle. \tag{4}$$

Here, B_i implies mixing through the magnetic field. As with the A coefficients, they are obtained from perturbation theory using, for example, the matrix given by Fowler *et al* (1973).)

In the lowest order (that is the effects of spin–orbit-coupling and $\boldsymbol{B}$) the matrix element of $(y \pm \mathrm{i}z)$ between ϕ_e and $|\Sigma_u;\ \alpha\rangle$ is non-zero. However, $I_+ - I_-$ vanishes. We have to go to the next order by expanding the largest term $a_1|s;\ \alpha\rangle$ with mixing terms. $a_1|s;\ \alpha\rangle$ becomes

$$a_1[(|s;\ \alpha\rangle - \mathrm{i}|s;\ \beta\rangle) + B_2|yz;\ \alpha\rangle]. \tag{5}$$

There is no spin–orbit coupling here, and therefore no terms containing A coefficients. For the first time, we obtain a non-zero MCDA signal originating from $|s;\ \beta\rangle$, which is present due to a perpendicular B component. The dipole moment between $|\Sigma_u;\ \alpha\rangle$ and ϕ_e that contributes to the non-zero MCPE is

$$ia_1[\pm\langle z;\ \beta|z|s;\ \beta\rangle - A_2\langle y;\ \beta|y|s;\ \beta\rangle]. \tag{6}$$

Collecting all contributions so far studied, we have $I_+ - I_- \neq 0$.

There are numerous terms contributing, which are not given explicitly here. It turns out that the non-zero MCPE is due to both the perpendicular $\boldsymbol{B}$ field and the spin–orbit coupling of the hole (coefficient A_2). For lighter halogens A_2 would be similar leading to an even smaller MCPE.

All terms other than (6) appear as complex conjugates for + and − polarizations, and therefore would not induce an MCPE until the above term is considered.

In summary:

(i) Both I_+ and I_- are 'strong', but there are many cancellations between I_+ and I_-.

(ii) The non-zero MCPE appears because we have included $|s;\ \beta\rangle$, which became mixed through $\boldsymbol{B}$ perpendicular to V_K. Also the spin–orbit coupling of the hole enters directly (see A_2 in (6)).

(iii) We have uncoupled the two electrons and considered the emission as a single-particle transition between the two one-electron states. This was done to account for the absence of the electron ODEPR signal. It could be that the excited electron is in a diffuse orbital or at a well separated location, for example.

(iv) If the system is some kind of an STE, then one should have observed an H centre rather than a V_K centre, which generally has different EPR parameters (g values). If we accept from the observed g value that it should be a V_K centre, then the electron should not be from an F centre, but more likely from Tl^0 as assumed.

(v) In the tunnelling recombination, electrons that had been trapped in the neighbourhood recombine with the V_K centre. Compared to the fast recombination of $\tau \simeq 1$ μs at 1.5 K observed under x-ray excitation, the long radiative life-time is determined by the slow electron tunnelling processes.

(vi) Although we have found parallel V_K centres in the MCDA we have not seen those in the MCPE. We think that this is due to the screening of the Tl^+ charge by the Tl 7s electron preventing the bending distortion as will be discussed in subsection 4.2 for the Tl-related V_{KA} centres observed in MCDA.

Our observations and the explanation show that the nature of the Tl-related luminescence can be understood as a kind of Tl-bound exciton (Smol'skaya and Koleszikova 1979). The observation that the tunnel recombination yields the same emission and ODEPR spectrum suggests that the hole is bound to Tl^+ and determines the recombination energy predominantly. It therefore seems that the alternative interpretation for the luminescence, that it is a Tl^+ intracentre transition (Masunaga *et al* 1965, Fowler 1969), can be ruled out by these experiments.

4.2. Tl-related V_K centres

As shown in the preceding section V_K centres produced by low-temperature x-irradiation were seen in the MCDA-detected ODEPR spectra. The fact that we observed parallel centres in ODEPR as well as perpendicular centres indicates that those V_K centres must have lost their axial symmetry. Otherwise we would have seen only perpendicular V_K centres as for example in KBr (see the detailed discussion on this point by Spaeth *et al* (1994)). The existence of the perturbation of the V_K centres is also seen in the satellite splitting of EPR lines of the parallel centres. We think that those EPR lines that look like the unperturbed ones from their hyperfine splitting pattern are formed by V_{KA} centres next to a Tl^+ ion in which the Tl^+ does not destroy the equivalence of the I nuclei, i.e. Tl^+ is in the mirror plane bisecting the two iodines (see figure 6(a)). However, the wave function has lost its axial symmetry about a [100] axis such that the optical transition loses its strict σ character along [100]. This acquired π character renders the MCDA non-zero also for parallel centres. The slightly increased HF splitting by 2 mT compared to the pure V_K centre (Pilloud and Jaccard 1975) also indicates this symmetrical bending.

As pointed out in the preceding section, the satellite splitting cannot be due to an HF interaction with either Tl^+ or Na^+. We think that it is caused by another V_K configuration in which e.g. the Ta^+ or Na^+ ions are located to one site of the V_K centre along its axis (figure 6(b)) such that the two I nuclei become inequivalent. Then, qualitatively, the degenerate M_I lines of the two equivalent nuclei can split. Probably there are more configurations of this nature. Their spectra are all superimposed. We therefore cannot perform a more precise analysis of the EPR spectra since there are too many possibilities of configurations and intensity ratios. It cannot be excluded either that two Tl^+ nor Na^+ ions are participating in the V_{KA} centre configurations.

This conjecture is also supported by the fact that we have seen at least six to seven MCDA bands in which the ODEPR spectra can be measured. From the detailed study of the V_K centres in KBr we know, that for strict axial symmetry and a mirror plane perpendicular to the bond axis of the two halogens—the unperturbed V_K symmetry—there should be two

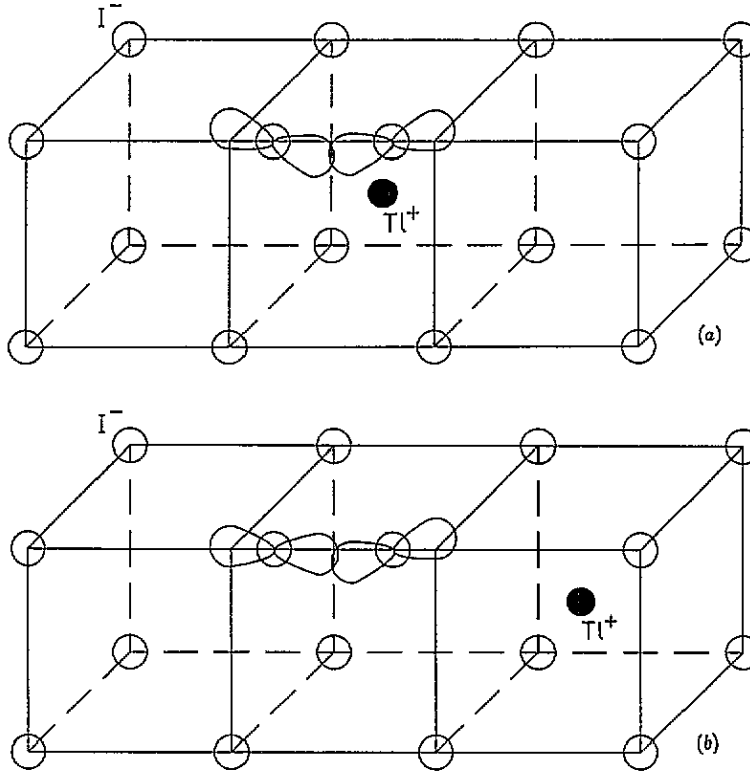

Figure 6. Models for Tl^+ perturbed V_{KA} centres: (a) the two I nuclei are 'equivalent'; (b) the two I nuclei are not 'equivalent'.

IR and one UV MCDA bands for the perpendicular centres. The fact that a second UV MCDA band was found was interpreted by assuming that the mirror-plane symmetry is lost by an asymmetric vibrational mode along the [110] axis. In the case of V_{KA} centres the loss of the mirror symmetry is probably caused by the Tl^+ or Na^+ perturbations. Then we would expect up to four MCDA bands for each configuration. Thus the MCDA spectrum found is a superposition of the spectra for at least two and probably more V_{KA} configurations, which cannot be separated by the tagging experiment because of the overlap of the EPR lines. The fact that at certain wavelengths (bands) only perpendicular V_K centres were observed (see figure 3(a) and section 2) indicates that unperturbed V_K centres have also been created for which the D_{2h} symmetry is not broken (Spaeth *et al* 1994).

The question arises of how V_{KA} centres can be formed at 4.2 K, where V_K centres are immobile. Thus it is not possible that V_K centres are formed in the pure lattice and then migrate to the Tl or other impurities. It is speculated that during the de-excitation of the excited electron–hole configuration at the Tl^+ not only does a radiative process occur, but also a non-radiative decay in which the electron and the hole are separated resulting in a Tl^+ perturbed V_K centre. The electron must have been captured at another electron trap, the usual procedure when creating V_K centres by x-irradiation even in the purest crystals (Fowler 1969). From the intensity ratio of the perpendicular-to-parallel centres in the EPR spectrum it is clear that the perturbed centres are not just a small fraction statistically produced at the Tl impurity. From the unperturbed V_K centres produced by x-irradiation

only the perpendicular ones are seen. It seems that in the Tl-doped crystals predominantly the Tl-perturbed V_K centres are produced at low temperature.

The strong signal of V_{KA} centres compared to the concentration of Tl may be due to the fact that the system is thermodynamically non-stable. Either Tl is more attractive for the hole to be associated with or the relaxation around is deeper and as a result the 'hot' holes are not trapped in a random way, but seek out the Tl centres preferentially. This is similar to what is observed in KBr doped with Na or Li. There also the luminescence band of the self-trapped exciton associated with the cation impurities is stronger than expected from their concentrations alone (Tanimura 1978, Tanimura *et al* 1982).

From an application point of view these findings are disappointing, because they imply that those V_{KA} centres found at the activator cannot be avoided by 'improving' the material. Of course, when electrons tunnel back or move back in a thermally activated motion at room temperature, those V_{KA} centres contribute to the afterglow effects, which occur during the room-temperature stability of a few minutes. It seems that CsI:Tl cannot be converted into an ideal scintillator crystal.

5. Conclusion

The observation of an MCPE of V_K centres and their EPR in the Tl-related x-ray luminescence band gives direct experimental evidence that the emission is an electron–hole recombination process in which the hole, being a V_K centre, seems to be part of an exciton-like excited state, of which the electronic part is not yet known in detail. The V_K centre is thought to be localized somewhere near the Tl^+ impurity; however, the axial- and inversion-symmetry properties of the V_K centre seem not to be affected measurably by this neighbourhood in contrast to those V_K centres created at low temperature and stabilized near Tl^+ as seen from our MCDA investigations. It is speculated that this difference may be due to the extra electron in a Tl orbital in the case of the excited 'exciton'-like state.

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