Optical properties of Tl²⁺ hole centres in alkali halides: I. Investigation with optical detection of paramagnetic resonance

U Rogulis†‖, J-M Spaeth†, I Cabria‡, M Moreno‡, J A Aramburu‡ and M T Barriuso§

† Universität-Gesamthochschule Paderborn, Fachbereich Physik, Warburger Strasse 100, D-33098 Paderborn, Germany
‡ Departamento Ciencias de la Tierra y Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain
§ Departamento Física Moderna, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

Abstract. The spectra of the magnetic circular dichroism of the absorption (MCDA) and of optically detected electron paramagnetic resonance (ODEPR) of Tl²⁺ hole centres have been investigated in a number of alkali halides. Several new absorption bands were found using excitation spectra of the Tl²⁺ ODEPR lines. The number of the MCDA transitions of Tl²⁺ in the bromides and especially in the iodides is larger than predicted by the molecular orbital picture discussed so far in the literature. An explanation will be given in part II by Cabria *et al* on the basis of MS–Xα calculations including the spin–orbit effects of the ligands.

1. Introduction

Tl⁺ activators in some x-ray storage phosphors such as RbI act as hole trap centres and form Tl²⁺ hole centres which, upon photostimulation, recombine with electrons liberated from the electron trap centres, i.e. F-centres (Rogulis *et al* 1996).

The microscopic structure of the Tl²⁺ hole centres was studied by electron paramagnetic resonance (EPR) in KCl by Dreybrodt and Silber (1967) and in KCl, RbCl and KBr by Frey *et al* (1975). Several optical absorption bands were reported for Tl²⁺ in KCl (Delbecq *et al* 1966), KBr (Roth and Halperin 1982) and KI (Hadley *et al* 1966, Hersh 1959, Kink 1968). The magnetic circular dichroism of the absorption (MCDA) of the UV absorption bands in KCl and KI have been measured by Beaumont *et al* (1973). They were interpreted as being due to s–p 'atomic-like' transitions, where the excited p orbitals of Tl²⁺ are split by the large spin–orbit interaction of thallium resulting in two resolved absorption bands. Several further absorption bands in the visible spectral region were observed in Tl²⁺ doped KI crystals (Hadley *et al* 1966, Hersh 1959), but no direct identification as being due to Tl²⁺ could be presented. Nistor *et al* (1994) reviewed the optical and EPR data available until 1994 as well as proposed models to explain the optical transitions of Tl²⁺ centres.

‖ Permanent address: Institute of Solid State Physics, University of Latvia, 8, Kengaraga Street, LV-1063 Riga, Latvia.

In our previous work we reported on the identification of several MCDA bands of Tl^{2+} centres in RbI using the MCDA excitation spectra measured in the Tl^{2+} EPR transition ('MCDA tagged by EPR', see Spaeth *et al* 1992). In this work we present a systematic study of the MCDA and MCDA-detected EPR of Tl^{2+} centres in six alkali halides. We detected many more transitions than previously reported elsewhere, which can clearly be associated with Tl^{2+} according to the experimental method used, in particular in the iodides in the low energy ('red') spectral region. For an understanding the existing molecular orbital (MO) models had to be extended. A theoretical interpretation will be presented in part II of the paper, by Cabria *et al* (1998).

2. Experimental details

The alkali halide crystals were grown with the Czochralski method and doped with 0.5 mol% Tl in the melt. The crystals were irradiated with x-rays (50 kV, 5 mA) *in situ* in the MCDA spectrometer for 1–2 hours. After irradiation at low temperatures, the temperature was, as a rule, increased beyond the temperature of the thermal stability of the V_K centres for about 5 min in order to diminish the amount of V_K centres and to increase the amount of the Tl^{2+} centres. However, irradiation at higher temperatures up to 300 K did not change the observed spectra.

The MCDA and MCDA-detected EPR spectra were measured with a custom-built computer-controlled spectrometer working in the K band (24 GHz) between 1.5 K and room temperature in the spectral range between 220 nm and about 1000 nm. Most measurements were performed at 1.5 K (for the method see e.g. Spaeth *et al* 1992). The sign of the MCDA is calibrated using the MCDA of the F-centre (Paus 1980) and presented such that positive values mean a right circular polarization.

3. Experimental results

The MCDA-detected EPR spectra of several x-irradiated Tl-doped alkali halides are shown in figure 1(a). One broad structureless EPR line appears at magnetic fields well above those corresponding to $g = 2$ ($\sim$850 mT). The lines are attributed to the $|1, -1\rangle \rightarrow |1, 0\rangle$ transition of the Tl^{2+} centre (Dreybrodt and Silber 1967) with the quantum numbers $F = 1$, $m_F = 0, \pm 1$ because of the large hyperfine (hf) interaction with the two magnetic isotopes ^{203}Tl (29.5% natural abundance) and ^{205}Tl (70.5% abundance) (see figure 1(b) for the level scheme). Both isotopes have $I = 1/2$ and very similar nuclear moments, such that they are not resolved in our MCDA-EPR spectra. No superhyperfine interactions with lattice neighbours could be resolved. The line positions are isotropic within experimental error. The second transition expected between $|1, 0\rangle$ and $|1, +1\rangle$ has not been observed in the K band in the available magnetic field range up to 3.5 T.

The Tl hf coupling constants A determined from the spectra by diagonalization of the appropriate spin Hamiltonian (Dreybrodt and Silber 1967) are collected in table 1. For the determination of the Tl hf interaction from the spectra we had to assume the g factors, since only one of the two transitions could be measured. For KCl, RbCl and KBr we used the g factors known from conventional EPR measurements. Our hf coupling constants A thus determined agree very well with those determined previously with conventional EPR (see table 1). A possible variation with temperature seems only small (our experiments were done at 1.5 K, previous EPR at 77 K). This is in line with the observation in the analogous system Cd^+ (s^1 configuration) in alkali halides where the temperature variation of A between 77 K and 4 K is only about 10^{-2} (Toyotomi and Onaka 1973).
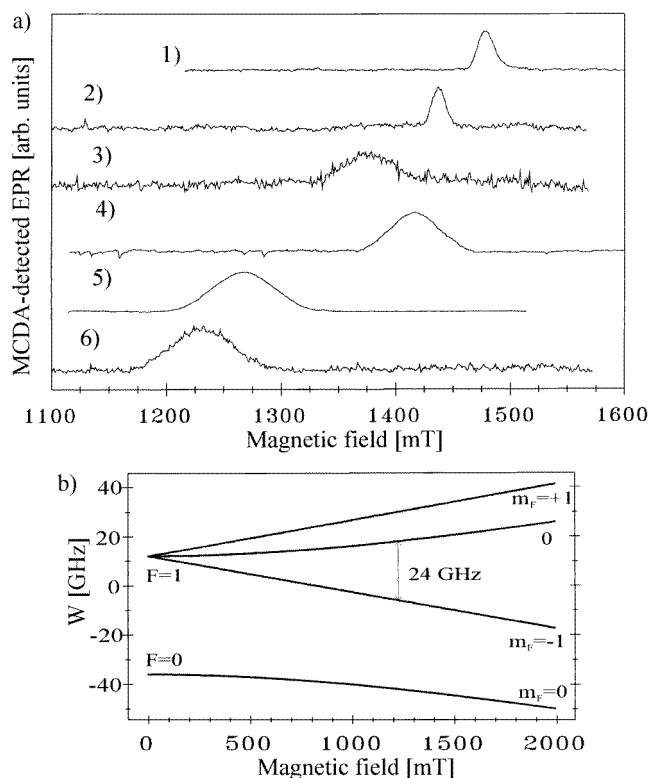
Figure 1. (a) MCDA-detected EPR spectra of the Tl^{2+} centres in six alkali halide crystals. The MCDA background has been subtracted. Measurements were made at $T = 1.5$ K and $B \parallel [100]$. Slightly different microwave frequencies were used: (1) KCl—23.9 GHz, (2) RbCl—23.7 GHz, (3) KBr—23.7 GHz, (4) RbBr—24.1 GHz, (5) KI—23.9 GHz, 6) RbI—23.7 GHz. (b) Breit–Rabi diagram for Tl^{2+} centre in RbI–Tl crystal with the g-factor of 2.1 and A (^{205}Tl) = 48 GHz.

For RbBr we used the same g factor as in KBr. According to the observation that g in KBr is larger than in KCl we assumed $g = 2.1$ in KI and RbI, a value somewhat larger than g in KBr. The resulting A values of Tl may have to be corrected, if better values of the g factors become available.

Figure 2 shows the MCDA bands obtained by measuring the MCDA excitation spectra of the Tl^{2+} resonance line shown in figure 1(a) for each alkali halide (in several cases the low energy bands were scaled up by a factor of 3 or 5 because of the low intensity of the original spectra). The peak positions of the MCDA bands measured are collected in table 2 together with those previously published and with the absorption band peaks. In all six alkali halide crystals we obtained a number of new MCDA bands besides the known bands in the UV. The largest number of bands (seven) was obtained in the iodides. All the bands are clearly due to Tl^{2+}, since in all bands the EPR of Tl^{2+} can be measured.

We observed an interesting feature of the lowest energy MCDA band in KI. The low energy MCDA band of the Tl^{2+} centre in KI at 1.6 eV is very similar in spectral shape and position to the MCDA band of the allowed 'red' transition of the V_K centre (Spaeth *et al* 1994). This similarity, however, seems to be fortuitous in view of the theoretical interpretation of the MCDA bands given by Cabria *et al* in part II.
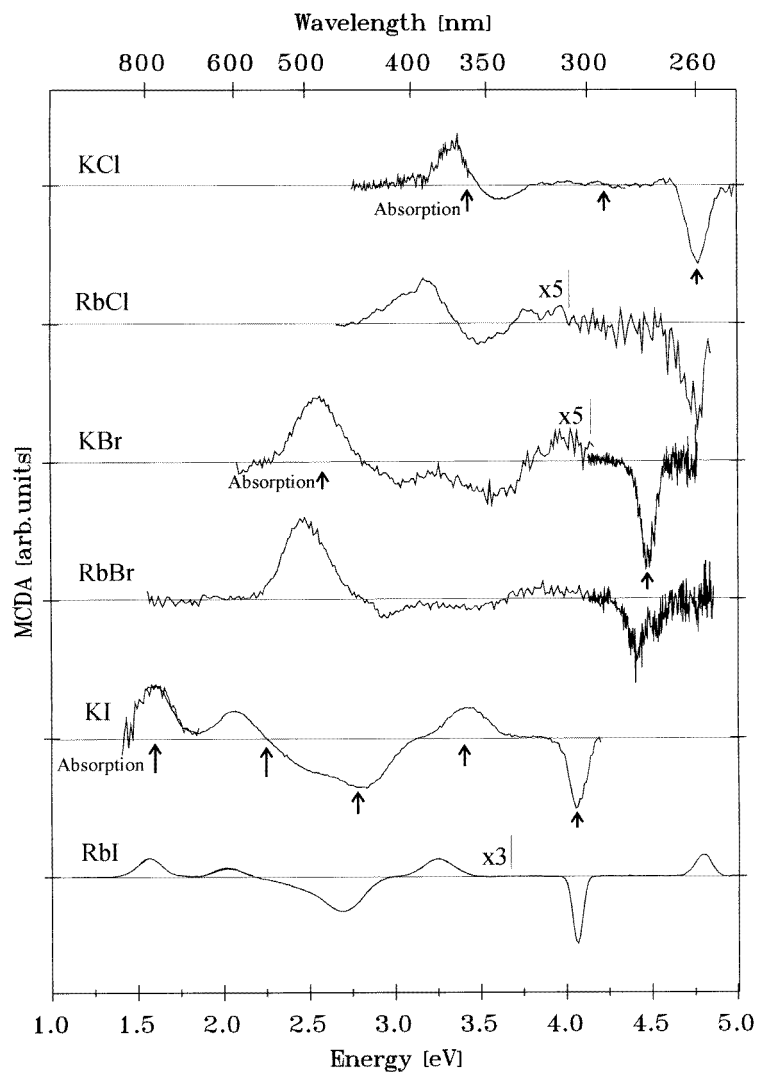
Figure 2. The spectra of the 'tagged MCDA' of the Tl^{2+} centres of six alkali halide crystals, measured at $T = 1.5$ K in the EPR lines of Tl^{2+}. For the RbCl, KBr and RbI crystals the low energy part of the spectra was scaled up.

4. Discussion

The electronic configuration of the Tl^{2+} centre is a $6s^1$ electron in an octahedral crystal field regarding the six nearest halogen neighbours: $Tl^{2+} X_6^{6-}$. The a_{1g} ground state is paramagnetic. The optical transition from the $^2S_{1/2}$ to the spin–orbit-split $^2P_{3/2}$ and $^2P_{1/2}$ excited states gives rise to the two UV transitions, of which except for RbI only the one with lower energy (to the $^2P_{1/2}$ state) is shown in figure 2. The reversal of signs in the MCDA bands in KI is typical for a spin–orbit-split excited state and has already been reported previously (Beaumont *et al* 1973). The splitting between the two UV transitions is 0.75 eV

Table 1. The ^{205}Tl hyperfine splitting parameters of the EPR and those obtained from the MCDA-EPR measurements for the Tl^{2+} centres of the alkali halides.

		g	A (Ghz)	Ref. for EPR
KCl	EPR	2.010	105.8	[b,c]
	MCDA-EPR	2.01[a]	110 ± 4	
RbCl	EPR	2.010	104.9	[c]
	MCDA-EPR	2.01[a]	103 ± 4	
Kbr	EPR	2.067	92.6	[c]
	MCDA-EPR	2.067[a]	93 ± 5	
RbBr	MCDA-EPR	2.067[a]	92 ± 5	
KI	MCDA-EPR	2.1[a]	52 ± 3	
RbI	MCDA-EPR	2.1[a]	48 ± 3	

[a] Assumption.
[b] Dreybrodt and Silber (1967).
[c] Frey *et al* (1975).

Table 2. Band positions of the MCDA bands and of the absorption bands of Tl^{2+} centres in six alkali halide crystals (values in eV).

KCl			
KCl	ABS	3.40; 4.22[a]	4.73; 5.63[a]
KCl	MCDA	3.35; 3.6; 4.05 (v. weak)	4.73; 5.67[b]
RbCl	MCDA	3.15; 3.50	4.75
KBr	ABS	2.58[c]	4.46[c]
KBr	MCDA	2.55; 3.05; 3.57; 4.0	4.48
RbBr	MCDA	2.48; 2.95; approx. 3.45; 3.9	4.40
KI	ABS	1.58; 2.25; 2.79; 3.42 [d−f]	4.06; 4.82 [d−f]
KI	MCDA	1.60; 2.07; 2.45; 2.8; 3.43	4.05; 4.82 [b]
RbI	MCDA	1.57; 2.03; approx. 2.35; 2.7; 3.25	4.07; 4.82

[a] Delbecq *et al* (1966).
[b] Beaumont *et al* (1973).
[c] Roth and Halperin (1982).
[d] Hadley *et al* (1966).
[e] Hersh (1959).
[f] Kink (1968).

in RbI and 0.9 eV in KCl, almost the reduced atomic value for the spin–orbit splitting of Tl (Beaumont *et al* 1973).

The question arises why one observes more transitions at lower energy. According to the model of Moreno (1979a, b) there are also hole transitions possible into the σ and π linear combinations of halogen p orbitals with t_{1u} symmetry (see figure 3) resulting in two further transitions. The MCDA spectra reveal changes of sign between the bands suggesting qualitatively that these two transitions are indeed four transitions because of transitions to spin–orbit-split σ and π linear combinations. For those one would expect a change of sign
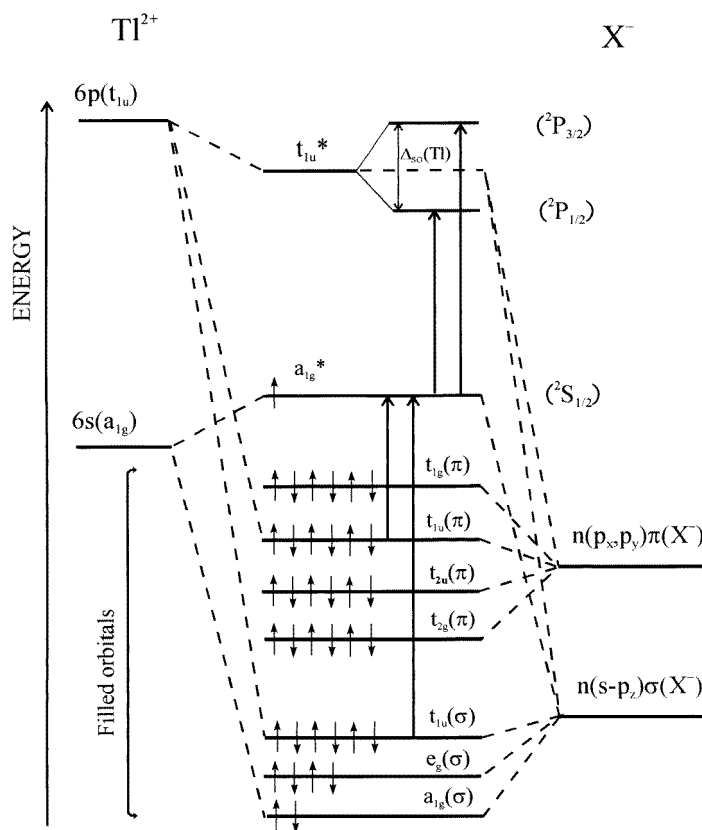
Figure 3. Qualitative energy level diagram of a [TlX$_6$] octahedral complex (after Nistor *et al* 1994, Ballhausen and Gray 1965, Moreno 1979a, b).

(Fowler 1968). The energy splittings between the positive and negative bands decrease on going from the iodides to the bromides and are hardly visible in the chlorides. This supports their interpretation, since the halogen spin–orbit splitting decreases strongly from the iodides to the chlorides. However, the number of five additional transitions in the iodides (altogether seven transitions) is not explained by such an energy level scheme.

An explanation of the observed MCDA spectra is presented in part II of the paper, by Cabria *et al* (1998), using an MS–Xα calculation and including the ligand spin–orbit effects.

Acknowledgments

References

Ballhausen C J and Gray H B 1965 *Molecular Orbital Theory* (New York: Benjamin) p 103
Beaumont J H, Hayes W and Laiho R T S 1973 *J. Phys. C: Solid State Phys.* **6** L479
Cabria I, Moreno M, Aramburu J A, Barriuso M T, Rogulis U and Spaeth J-M 1998 *J. Phys.: Condens. Matter* **10** 6481

Delbecq C J, Ghosh A K and Yuster P H 1966 *Phys. Rev.* **151** 599

Dreybrodt W and Silber D 1967 *Phys. Status Solidi* **20** 337

Fowler W B 1968 *The Physics of Color Centers* ed W B Fowler (New York: Acdemic) ch 2, p 125

Frey W, Huss R, Seidel H and Werkmann E 1975 *Phys. Status Solidi* b **68** 257

Hadley W B, Polick S, Kaufman R G and Hersh H N 1966 *J. Chem. Phys.* **45** 2040

Hersh H N 1959 *J. Chem. Phys.* **31** 909

Kink R A 1968 *Doctoral Thesis* Tartu

Moreno M 1979a *J. Phys. C: Solid State Phys.* **12** L921

——1979b *Solid State Commun.* **29** 653

Nistor S V, Schoemaker D and Ursu I 1994 *Phys. Status Solidi* b **185** 9

Paus H J 1980 *Habilitationsschrift* Universität Stuttgart

Rogulis U, Dietze C, Pawlik Th, Hangleiter Th and Spaeth J M 1996 *J. Appl. Phys.* **80** 2430

Roth M and Halperin A 1982 *J. Phys. Chem. Solids* **43** 609

Spaeth J M, Meise W and Song K S 1994 *J. Phys.: Condens. Matter* **6** 1801

Spaeth J M, Niklas J R and Bartram B H 1992 *Structural Analysis of Point Defects in Solids (Springer Series in Solid State Sciences 43)* (Berlin: Springer)

Toyotomi Y and Onaka R 1973 *J. Phys. Soc. Japan* **34** 623