Effects of Temperature and Magnetic Fields on the Luminescence of Single Crystal $(NH_4)_2TeCl_6$

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The optical absorption of $(NH_4)_2TeCl_6$ in acetonitrile at room temperature and the luminescence (spectra, decay curves) of single crystal $(NH_4)_2TeCl_6$ at $1.9\,K \leq T \leq 180\,K$ and at applied magnetic fields $\boldsymbol{H}$ $(0 \leq H \leq 6\,T)$ are reported. The temperature dependence of the luminescence indicates the existence of a metastable excited state energetically by $\sim 80\,cm^{-1}$ below a second excited state. With $\boldsymbol{H} \parallel \langle 111 \rangle$ the decay curves are monoexponential with magnetic field dependent slopes. $\boldsymbol{H} \parallel \langle 001 \rangle$ yields biexponential decay curves, each composed of a slow component corresponding to the decay at $H = 0$, and of a field dependent fast component. The experimental results can be explained by effects of a tetragonal Jahn-Teller distortion due to a strong coupling of the excited electronic state $^3T_{1u}$ of the Te(IV) ions and E_g vibration modes.

1. Introduction

The optical properties of octahedrally coordinated s^2 ions in host lattices have been investigated extensively [1, 2]. Monovalent s^2 ions (like In^+ and Tl^+) substituted in alkali halides occupy sites of perfectly cubic symmetry. In order to study divalent and trivalent s^2 ions (like Sn^{2+}, Pb^{2+} and Sb^{3+}, Bi^{3+}, respectively) at sites of cubic symmetry, the alkali halides are not appropriate as host lattices, since charge compensation effects can destroy the cubic site symmetry [3–5]. In these cases other compounds have to be used as host lattices; e.g. the cubic elpasolites Cs_2NaMX_6 (with M = Sc, Y, La and X = Cl, Br) containing $[MX_6]^{3-}$ octahedra of cubic symmetry are suited as host lattices for Sb^{3+} and Bi^{3+} ions [6–8].

For several s^2 ions at sites of cubic symmetry a Jahn-Teller (JT) effect due to a coupling of the lowest excited triplet state (derived from the electron configuration s^1p^1) and the E_g and T_{2g} vibrational modes could be established [9–11]. The strong magnetic field effects on the luminescence decay properties of monovalent s^2 ions [12–16] and Sb^{3+} ions [17] at sites of cubic symmetry in host lattices are closely associated with this JT effect.

The purpose of this paper is to report on the temperature dependence and the magnetic field dependence of the luminescence of tetravalent s^2 ions at sites of cubic symmetry. The Te(IV) ion seems to be appropriate to such an investigation. Both in host lattices (like Cs_2HfCl_6) and in non-diluted hexahalogenotellurates(IV) like Cs_2TeCl_6 the Te(IV) ions occupy sites of symmetry O_h [18, 19]. Although a static deformation of a $[TeCl_6]^{2-}$ octahedron in its electronic ground state does not exist, a dynamical JT effect for excited states has been found by Stufkens from an analysis of the optical absorption spectra [20, 21]. From the dependence of the luminescence of single crystal $(NH_4)_2TeCl_6$ on temperature and external magnetic fields informations on the energetical order of the lowest excited states and on the type of JT distortions of the $[TeCl_6]^{2-}$ octahedra are expected.

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2. Experimental

The compound $(NH_4)_2TeCl_6$ has been prepared according to the method described in [22]. To avoid decomposition of the crystal surfaces by atmospheric humidity, the samples were coated with paraffin oil. The size of the samples for the spectroscopic measurements was $\sim 1 \times 1 \times 0.5\,mm^3$.

For the excitation of the luminescence spectra the 364 nm line of an argon ion laser with polarization parallel to the $\langle 001 \rangle$-axis of the crystals has been used. The emission lifetimes were measured by the multichannel scaling method. The applied exciting light (337.1 nm line of a nitrogen laser) had a repetition rate of 20 Hz and a pulse width of ~ 3 ns. A liquid

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helium bath cryostat of a superconducting magnet system (Oxford Company, SM 4) has been employed for the measurement of the luminescence at different temperatures ($1.9\,K \leq T \leq 180\,K$) and magnetic field strengths ($0 \leq H \leq 6\,T$). The luminescence radiation was analyzed by a Spex double-grating monochromator and detected by an EMI photomultiplier with S 20 cathode.

The absorption spectrum of $(NH_4)_2TeCl_6$ dissolved in acetonitrile (Merck Uvasol for spectroscopy) has been recorded by a Shimadzu spectrometer (210 UV).

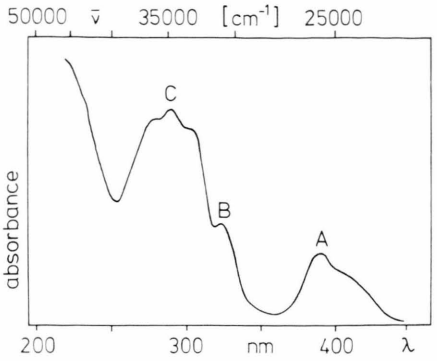

Fig. 1. Absorption spectrum of $(NH_4)_2TeCl_6$ dissolved in acetonitrile. $c = 1.5 \times 10^{-4}$ mole $\cdot l^{-1}$. $T \approx 295\,K$.

3. Results

Absorption spectrum

Figure 1 shows the absorption spectrum of $(NH_4)_2TeCl_6$ dissolved in acetonitrile at room temperature. In the low energy range three bands are observed: the A band with a doublet structure (maxima at $24\,300\,cm^{-1}$ and $25\,700\,cm^{-1}$), the relatively weak B band (maximum at $\sim 30\,700\,cm^{-1}$), and the C band with a triplet structure (maxima at $32\,700\,cm^{-1}$, $34\,500\,cm^{-1}$; $36\,500\,cm^{-1}$; $\varepsilon_{max} \sim 9000\,mol^{-1}\,cm^{-1} \cdot l$). The shape of the absorption spectrum is in agreement with that reported by Stufkens et al. [20–21].

Luminescence Spectrum

The luminescence spectrum of single crystal $(NH_4)_2TeCl_6$ has been measured between $T = 1.9\,K$ and 180 K. At higher temperatures the intensity was below the limit of detection. The luminescence exhibits no polarization effects. The spectrum consists of one broad band, as shown in Fig. 2 for $H = 0$. At $T = 1.9\,K$ the emission maximum has the energy $\bar{\nu} = 15\,530\,cm^{-1}$. Raising the temperature to $T = 150\,K$ shifts the maximum by $\sim 300\,cm^{-1}$ to the blue. Between $T = 1.9\,K$ and 40 K the integral intensity of the luminescence grows by a factor of ~ 6.5, between $T = 40\,K$ and 100 K it is nearly constant, and with further increase of the temperature the intensity decreases to the limit of detection (at $T = 180\,K$), cf. Figure 3.

The luminescence spectrum of $(NH_4)_2TeCl_6$ can be influenced by external magnetic fields $\boldsymbol{H}$. For the orientations $\boldsymbol{H} \parallel \langle 001 \rangle$ and $\boldsymbol{H} \parallel \langle 111 \rangle$ the same effects on the spectrum have been observed. The effects depend on the relative orientation of $\boldsymbol{H}$ and the electric field vector $\boldsymbol{E}$ of the emitted light. From Fig. 2 it can be seen that for $\boldsymbol{E} \parallel \boldsymbol{H}$ the intensity of the luminescence at

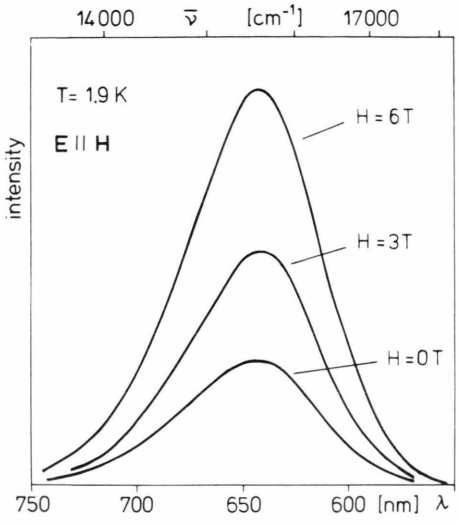

Fig. 2. Luminescence spectra of single crystal $(NH_4)_2TeCl_6$ at magnetic field strengths $H = 0$, 3 T and 6 T. $\boldsymbol{E} \parallel \boldsymbol{H}$. $T = 1.9\,K$. $\lambda_{exc} = 364\,nm$.

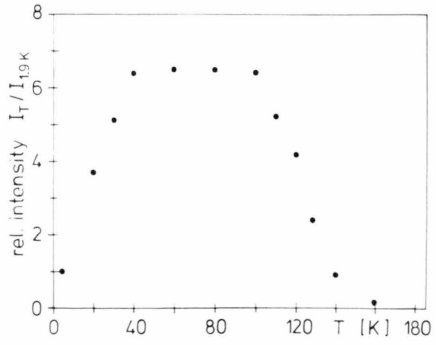

Fig. 3. Relative luminescence intensity, $I_T/I_{T=1.9\,K}$, of single crystal $(NH_4)_2TeCl_6$ as a function of temperature T. $\lambda_{exc} = 364\,nm$.

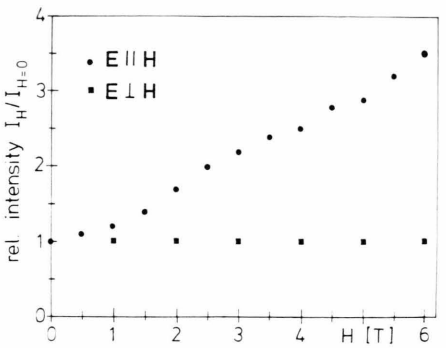

Fig. 4. Relative luminescence intensities, $I_H/I_{H=0}$, of single crystal $(NH_4)_2TeCl_6$ as functions of magnetic field strength H for polarizations $\boldsymbol{E} \parallel \boldsymbol{H}$ and $\boldsymbol{E} \perp \boldsymbol{H}$, respectively. $T = 1.9$ K. $\lambda_{exc} = 364$ nm.

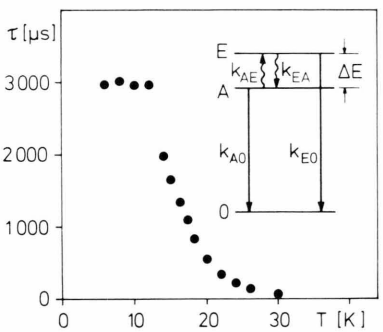

Fig. 5. Luminescence decay time τ of single crystal $(NH_4)_2TeCl_6$ as a function of temperature T. $\lambda_{exc} = 337.1$ nm.

$T = 1.9$ K increases by a factor of ~ 3.5, if the magnetic field strength is raised from $H = 0$ to 6 T. The energy of the emission maximum, however, is not affected. For $\boldsymbol{E} \perp \boldsymbol{H}$ no magnetic field effect on the luminescence spectrum has been observed. Figure 4 shows that the relative integral intensity, $I_H/I_{H=0}$, increases nearly linearly with the magnetic field strength for $\boldsymbol{E} \parallel \boldsymbol{H}$, but it is independent of H for $\boldsymbol{E} \perp \boldsymbol{H}$.

Luminescence Decay

The luminescence decay at $H = 0$ is independent of the polarization. All measured decay curves are monoexponential. Temperature increase from $T = 1.9$ K to 30 K reduces the luminescence decay time $\tau_{H=0}$ by a factor of ~ 50, cf. Figure 5. The temperature dependence of $\tau_{H=0}$ can be described by the equation

$$\frac{1}{\tau_{H=0}} = \frac{k_{A0} + 2k_{E0} \cdot \exp(-\Delta E/kT)}{1 + 2 \cdot \exp(-\Delta E/kT)} \qquad (1)$$

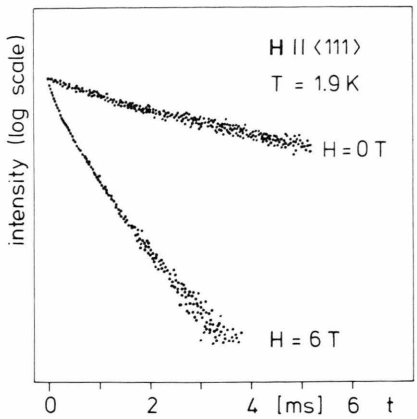

Fig. 6. Luminescence decay curves of single crystal $(NH_4)_2TeCl_6$ at $H = 0$ and at $H = 6$ T with $\boldsymbol{H} \parallel \langle 111 \rangle$, respectively. $T = 1.9$ K. $\lambda_{exc} = 337.1$ nm.

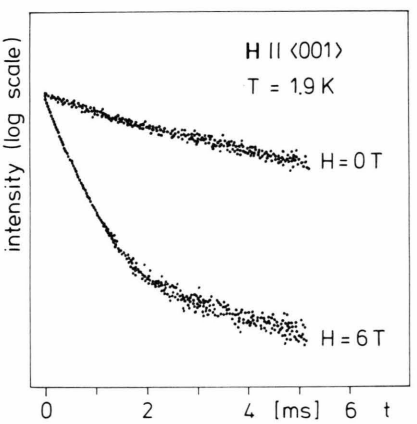

Fig. 7. Luminescence decay curves of single crystal $(NH_4)_2TeCl_6$ at $H = 0$ and at $H = 6$ T with $\boldsymbol{H} \parallel \langle 001 \rangle$, respectively. $T = 1.9$ K. $\lambda_{exc} = 337.1$ nm.

with $\tau_{H=0}^{-1} = k_{A0}$ for $kT \ll \Delta E$ and $\tau_{H=0}^{-1} = k_{E0}$ at $kT \gg \Delta E$. Fitting of the experimental data yields $k_{A0} = (330 \pm 20)\,s^{-1}$, $k_{E0} = (7 \pm 1) \cdot 10^5\,s^{-1}$, and $\Delta E = (80 \pm 10)\,cm^{-1}$.

An applied magnetic field $\boldsymbol{H}$ changes the luminescence decay depending on the relative orientation of $\boldsymbol{H}$ and the crystal axes. Figure 6 shows the decay curves for $\boldsymbol{H} \parallel \langle 111 \rangle$ at $H = 0$ and $H = 6$ T, respectively. They are roughly straight lines, indicating an approximately monoexponential behavior. The decay becomes faster with increasing magnetic field strength H. Magnetic fields with $\boldsymbol{H} \parallel \langle 001 \rangle$ yield a distinctly different behavior of the decay, cf. Figure 7.

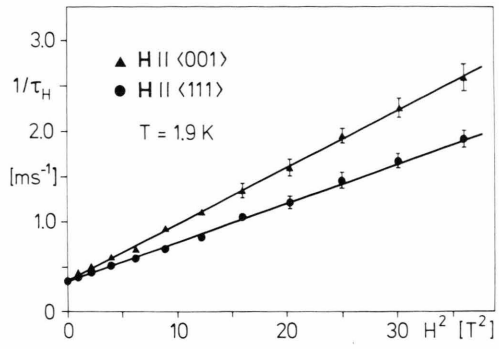

Fig. 8. Luminescence deactivation rate $1/\tau_H$ of single crystal $(NH_4)_2TeCl_6$ as a function of the square of the magnetic field strength H with $\boldsymbol{H} \| \langle 111 \rangle$ and $\boldsymbol{H} \| \langle 001 \rangle$, respectively. $T = 1.9$ K. $\lambda_{exc} = 337.1$ nm.

The decay curve at $H = 6$ T is composed of a fast component, which is monoexponential and has the same slope as the decay curve with $\boldsymbol{H} \| \langle 111 \rangle$ at $H = 6$ T, and a slow component, which is parallel to the decay curve at zero field. Figure 8 shows the luminescence deactivation rate $1/\tau_H$ versus H^2 for $\boldsymbol{H} \| \langle 111 \rangle$ and $\boldsymbol{H} \| \langle 001 \rangle$. The plots are straight lines, and the ratio of their slopes, $R = S(111)/S(001)$, has a value of 1.4 ± 0.2. Figure 8 indicates that $1/\tau_H - 1/\tau_{H=0}$ is a purely quadratic function of H,

$$1/\tau_H - 1/\tau_{H=0} \sim H^2 .$$

4. Discussion

The light-yellow compound $(NH_4)_2TeCl_6$ forms crystals of cubic symmetry with the space group $Fm3m(O_h^5)$ [23]. The $[TeCl_6]^{2-}$ octahedra have perfect O_h symmetry.

Neglecting spin-orbit coupling, the electronic ground state and the first excited states of an octahedrally coordinated Te^{4+} ion are $^1A_{1g}(5s^2)$ and $^3T_{1u}$, $^1T_{1u}(5s^1 6p^1)$, respectively. Spin-orbit coupling splits the $^3T_{1u}$ into A_{1u}, T_{1u}, E_u, and T_{2u}. For electric dipole transitions the process $A_{1g} \rightarrow T_{1u}(^1T_{1u})$ is allowed and yields the C band of the absorption spectrum. The transitions $A_{1g} \rightarrow T_{1u}(^3T_{1u})$ (partly allowed by spin-orbit mixing of $^3T_{1u}$ and $^1T_{1u}$) and $A_{1g} \rightarrow E_u, T_{2u}(^3T_{1u})$ (partly allowed by vibronic coupling) give rise to the bands A and B, respectively. The transition $A_{1g} \rightarrow A_{1u}(^3T_{1u})$ has not been observed in the absorption spectrum. It is electric dipole forbidden. By a dynamical JT effect (interaction of the T_{1u} states with E_g and T_{2g} vibrational modes), the C band and A band split into a triplet and doublet band system, respectively [9–11].

To describe the properties of the luminescence of $(NH_4)_2TeCl_6$, especially the observed magnetic field effects, we adopt a model developed by Simkin et al. [14–16] to analyze the $^3T_{1u}$ states of s^2 ions in the KI lattice.

Assuming a strong coupling of the orbital triplet T_{1u} with T_{2g} vibrational modes, four equivalent stable trigonal distortions (JT wells) along the directions $\langle 111 \rangle$, $\langle \bar{1}\bar{1}1 \rangle$, $\langle \bar{1}1\bar{1} \rangle$, and $\langle 1\bar{1}\bar{1} \rangle$ result. These four orbital states are spin triplets. By dipole-dipole interaction and spin-orbit coupling the degeneracy of each spin triplet is partly removed. A spin singlet A below a spin doublet E results. A is the most stable relaxed excited state (RES) [16].

Coupling of the orbital triplet T_{1u} with E_g vibrational modes leads to three equivalent stable tetragonal distortions (JT wells) with orientations $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$. Each of these spin triplets is also split into a spin doublet E and a RES A [15]. The energies of the tetragonal and trigonal JT wells are expected to be different.

Electric dipole transitions between E and the ground state are allowed. A radiative deactivation of the RES A is forbidden, both for trigonal and for tetragonal distortions, however, it can get a very small transition probability by hyperfine interactions [24] and by phonon assisted coupling [25] of the RES A with the corresponding spin doublet E.

The observed luminescence of $(NH_4)_2TeCl_6$ and its temperature dependence are compatible with this model and with (1). At low temperature, the luminescence corresponds to the transition from states A to the ground state with a large decay time $\tau_H = k_{A0}^{-1}$ of ~ 3 ms. The twofold degenerate spin doublet E has an energy higher by $\Delta E \sim 80\,cm^{-1}$. By increase of temperature the states E become thermally populated. Because of their large deactivation rate, $k_{E0} \sim 7 \cdot 10^5\,s^{-1}$, the luminescence decay time decreases and approaches the high temperature value $\tau_E = k_{E0}^{-1} \sim 1\,\mu s$ with increasing temperature, cf. Figure 5. Equation (1) describes the corresponding three level system shown in the insert of Figure 5. The following assumptions have to be made: $k_{AE} = k_{EA} \cdot \exp(-\Delta E/kT)$, $k_{EA} \gg k_{E0}$, and $k_{E0} \gg k_{A0}$.

The increase of the luminescence intensity between $T = 1.9$ K and 40 K is a consequence of the growing thermal population of the state E, which has a higher

quantum yield than A. With further increase of temperature the radiative deactivation of the state E dominates the luminescence and, additionally, nonradiative processes deactivate more and more the excited states. Thus, the intensity is nearly constant between $T = 40\,K$ and $100\,K$ and decreases at higher temperatures.

As described above, two types of JT wells can occur. Whether the emitting states belong to trigonal or tetragonal JT wells or to both types cannot be deduced from the luminescence spectra and the decay behavior at $H = 0$.

From the magnetic field dependence of the luminescence, however, it follows immediately that the RES A are due to tetragonal JT wells. An applied magnetic field $\boldsymbol{H}$ interacts with a spin $\boldsymbol{S}(S_x, S_y, S_z)$ correspondingly to the energy operator

$$H_{\text{pert}} = \mu_B H [g_\perp (\alpha S_x + \beta S_y) + g_\parallel \gamma S_z],$$

with μ_B the Bohr magneton, $g_\perp = g_x = g_y$, and $g_\parallel = g_z$. (α, β, γ) are the direction cosines in the (x, y, z) coordinate system. With $H \approx 6\,T$ and $g \approx 2$ it follows $\mu_B \cdot H \cdot g \approx 6\,cm^{-1}$. An energy shift of this order can not be revealed in the luminescence spectra considering the large halfwidth of the emission band.

As the experiments have shown, an external magnetic field can change strongly the radiative deactivation rate, cf. Figure 8. The observed effects result from a magnetic field induced coupling of the RES A with the corresponding spin doublets E. First order perturbation theory yields

$$|A\rangle_H \approx |A\rangle_{H=0} + \frac{i g_\perp \mu_B H}{\Delta E} [c_1 |E_1\rangle + c_2 |E_2\rangle]. \quad (2)$$

$g_\perp$ is the component of the g factor perpendicular to the respective JT distortion. The coefficients c_1 and c_2 of the doublet wavefunctions $|E_1\rangle$ and $|E_2\rangle$ depend on the direction cosines α, β, γ. They vanish if the magnetic field $\boldsymbol{H}$ is parallel to the JT distortion [12–16].

Via the mixing coefficient in (2), the luminescence decay time of the RES A becomes a function of H:

$$\frac{1}{\tau_A(H)} = \frac{1}{\tau_A} + \lambda \left(\frac{g_\perp \mu_B H}{\Delta E} \right)^2 \cdot \frac{1}{\tau_E}. \quad (3)$$

τ_A and τ_E are the luminescence decay times of the states A and E at $H = 0$. The factor λ depends on the relative orientation of $\boldsymbol{H}$ and the JT distortion. For trigonal and tetragonal JT wells and for the magnetic field orientations $\boldsymbol{H} \parallel \langle 001 \rangle$ and $\boldsymbol{H} \parallel \langle 111 \rangle$ the values of λ are summarized in Table 1.

Table 1. Values of the λ factor for tetragonal and trigonal JT distortions at magnetic field orientations $\boldsymbol{H} \parallel \langle 001 \rangle$ and $\boldsymbol{H} \parallel \langle 111 \rangle$.

$\boldsymbol{H} \parallel \langle 001 \rangle$				$\boldsymbol{H} \parallel \langle 111 \rangle$			
tetrag.	λ	trig.	λ	tetrag.	λ	trig.	λ
$\langle 100 \rangle$	1	$\langle 111 \rangle$	2/3	$\langle 100 \rangle$	2/3	$\langle 111 \rangle$	0
$\langle 010 \rangle$	1	$\langle \bar{1}\bar{1}1 \rangle$	2/3	$\langle 010 \rangle$	2/3	$\langle \bar{1}\bar{1}1 \rangle$	8/9
$\langle 001 \rangle$	0	$\langle \bar{1}1\bar{1} \rangle$	2/3	$\langle 001 \rangle$	2/3	$\langle \bar{1}1\bar{1} \rangle$	8/9
		$\langle 1\bar{1}\bar{1} \rangle$	2/3			$\langle 1\bar{1}\bar{1} \rangle$	8/9

Trigonal JT distortions: With $\boldsymbol{H} \parallel \langle 001 \rangle$ the decay times of all four JT wells have the same magnetic field dependence ($\lambda = 2/3$). Thus the resulting decay curve is monoexponential and depends on H. With $\boldsymbol{H} \parallel \langle 111 \rangle$ the decay is biexponential. For one JT well ($\lambda = 0$) a field independent decay time $\tau_A(H) = \tau_A$ results, whereas the decay due to the other three JT wells depends on H with $\lambda = 8/9$.

Tetragonal JT distortions: A biexponential decay (one JT well with $\lambda = 0$ and two JT wells with $\lambda = 1$) is expected for $\boldsymbol{H} \parallel \langle 001 \rangle$. The orientation $\boldsymbol{H} \parallel \langle 111 \rangle$ yields a magnetic field dependent monoexponential decay (three JT wells with $\lambda = 2/3$).

The experimental results shown in Figs. 6 and 7 are clearly in agreement with the predictions for tetragonal JT distortions. The same result can be deduced from the slopes S of the plots $1/\tau_H$ over H^2 for $\boldsymbol{H} \parallel \langle 001 \rangle$ and $\boldsymbol{H} \parallel \langle 111 \rangle$, respectively, cf. Figure 8. According to (3) the ratio of the slopes $S(001)$ and $S(111)$ can be written as $\lambda(001)/\lambda(111)$ with the values 0.75 and 1.5 for trigonal and tetragonal JT distortions, respectively. The experimental value is 1.4 ± 0.2, confirming that the luminescence originates from tetragonal JT distortions.

A magnetic field $\boldsymbol{H}$ perpendicular to a tetragonal JT distortion reduces the symmetry of the system to C_{2h}. The orientation of $\boldsymbol{H}$ defines the z axis in the subgroup. At this lower symmetry, electric dipole transitions from the RES A to the ground state are allowed with z-polarization. Therefrom the selection rule $\boldsymbol{E} \parallel \boldsymbol{H}$ results.

From (3) it follows that the magnetic field dependent part of the decay rate is a purely quadratic function of H.

From the experimental values of the slopes $S = \lambda(g_\perp \mu_B/\Delta E)^2/\tau_E$, $g_\perp$-values of 1.7 ± 0.6 (for $\boldsymbol{H} \parallel \langle 111 \rangle$) and 1.3 ± 0.4 (for $\boldsymbol{H} \parallel \langle 001 \rangle$) result. For the case that the JT interaction is much stronger than the spin-orbit coupling, the theory predicts (with $S = 1$) a g-value of 2. For the contrary case (with $J = L = S = 1$) the g-value is 1.5 [16]. These calculated values can be reduced by spin-orbit mixing of $^1T_{1u}$ and $^3T_{1u}$. The experimental g-values indicate that in the $[TeCl_6]^{2-}$ octahedra an intermediate case of coupling is effective.

Acknowledgement

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