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## The relaxed excited state responsible for the luminescence associated with the forbidden transition in $\text{KI:Sn}^{2+}$ crystals

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**Abstract.** The lifetime of luminescence in  $\text{KI:Sn}^{2+}$  crystals has been investigated using a streak camera. By excitation in the absorption band B due to a dipole-forbidden  $^1\text{S}_0 \rightarrow ^3\text{P}_2$  transition in the  $\text{Sn}^{2+}$  centre, an emission band with a peak at 446 nm is produced by the reverse transition  $^3\text{P}_2 \rightarrow ^1\text{S}_0$ . The emission B has a lifetime of 27.4 ns at 15 K and its lifetime decreases with increasing temperature. Such a short lifetime, which was unexpected for the originally forbidden band, is explained by a displacement of the vacancies around  $\text{Sn}^{2+}$  ions in the relaxed excited state which gives rise to a mixing of the forbidden  $^3\text{P}_2$  states with the allowed  $^1\text{P}_1$  state.

### 1. Introduction

One compact and useful way of visualizing the process of optical absorption and emission for defect centres in solids is obtained using a configuration coordinate diagram such as the energy diagram shown in figure 1 (see, e.g., the book by Henderson and Imbusch (1989)). In terms of this diagram, one can explain the Stokes shift, and the absorption and emission band widths of the absorption and emission bands if we assume the Franck–Condon principle that the lattice coordinates do not change during the optical transition between the ground and excited states.

In optical absorption, an electron moves from the ground state into the excited state ( $A \rightarrow B$  in figure 1) under a fixed lattice coordinate  $Q_G$ . The optical transition provides a new wavefunction and spatial distribution of the electron, giving rise to strong lattice vibrations and subsequent relaxation into a new electron–lattice configuration C at the equilibrium position  $Q_E$ , which is called the relaxed excited state. On the other hand, the excited state B responsible for absorption is called the unrelaxed excited state. After the mean lifetime, the excited electron returns radiatively from the relaxed excited state to the unrelaxed ground state D. The emission transition ( $C \rightarrow D$ ) is followed by rapid relaxation from the state D into the initial normal (relaxed) ground state A, completing the optical cycle. The properties of the relaxed excited state are studied by the radiative electron transition  $C \rightarrow D$ , i.e. the emission spectrum and lifetime measurement.

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In solids, in addition to dipole-allowed absorption bands, absorption bands due to the electronic transition which is forbidden by the selection rules have sometimes been observed since its prohibition is relaxed by the lattice vibration. The relaxed excited state of the 'forbidden' band is expected to be different from the electronic state of the unrelaxed excited state because of a strong electron-lattice interaction during the relaxation process. In this paper we examine the relaxed excited state of the 'forbidden' band using the example of a dipole-forbidden absorption band in an  $s^2$  ion centre in alkali halides.

Alkali-halide crystals containing a small amount of  $s^2$  configuration ions such as  $\text{Sn}^{2+}$ ,  $\text{In}^+$  and  $\text{Tl}^+$  exhibit four absorption bands, denoted A, B, C, and D in order of increasing energy, on the low-energy side of the lowest exciton band due to the bulk alkali halides (see, e.g., review articles by Hizhnyakov and Kristoffel (1984) and Jacobs (1991)). Bands A, B and C are due to electronic transition  $s^2 \rightarrow sp$  in the  $s^2$  ion, while band D is due to charge transfer. Band A is attributed to the spin-orbit-allowed transition  $^1S_0 \rightarrow ^3P_1$  ( $^1A_{1g} \rightarrow ^3T_{1u}$  in a cubic crystal field), while band C is due to the dipole-allowed transition  $^1S_0 \rightarrow ^1P_1$  ( $^1A_{1g} \rightarrow ^1T_{1u}$ ). Band B is due to the dipole- and spin-forbidden  $^1S_0 \rightarrow ^3P_2$  ( $^1A_{1g} \rightarrow ^3T_{2u}$  and  $^3E_u$ ), but it is allowed by the lattice vibration. Therefore the intensity of band B increases with increasing temperature although it is the smallest of the four bands (Tsuboi *et al* 1973). The excitation in band A or B leads to the emission band due to the reverse transitions  $^3P_1 \rightarrow ^1S_0$  and  $^3P_2 \rightarrow ^1S_0$ , which are called emission band A and emission band B, respectively. In  $\text{KI}:\text{Sn}^{2+}$ , the broad doublet-structured band which appears in the 490–600 nm region is known as emission band A (Fukuda 1970a, Kamishina *et al* 1980), while the single emission band with a peak at 446 nm is emission band B (Fukuda 1970b). Therefore we study the 446 nm emission and its decay time here to clarify the properties of the emission band associated with the forbidden transition.

## 2. Experimental procedure and experimental results

Single crystals of  $\text{KI}:\text{Sn}^{2+}$  (0.01 mol% in the melt) were grown by the Stockbarger method. The crystals were heated at 500 °C for 30 min and quenched to room temperature on a copper plate immediately before the measurement to avoid the formation of aggregate  $\text{Sn}^{2+}$  centres. The crystals were excited by a Moletron UV14  $\text{N}_2$  laser. Band B for  $\text{KI}:\text{Sn}^{2+}$  is located in the region 310–340 nm (Tsuboi *et al* 1974, Tsuboi 1981). Therefore,  $\text{N}_2$  laser light of 337.1 nm wavelength leads to excitation in band B. The pulse width of the laser is 4 ns, and its peak power is 425 kW. The crystal luminescence was collimated, from the direction perpendicular to the exciting light, to an entrance slit of a Jobin-Yvon HR 320 polychromator where a ruled grating (size 68 mm  $\times$  68 mm) with a groove density of 100 g  $\text{mm}^{-1}$  and a blaze wavelength of 450 nm is installed. The exit slit width was fixed at 15 mm. The luminescence intensity was detected with a Hamamatsu Photonics C2830 streak camera attached to a Hamamatsu Photonics Peltier-element-cooled charge-coupled device photodetector. It was possible to synchronize the laser pulse with the streak sweep within a jitter of less than 2 ns. The luminescence decay and time-resolved spectrum were obtained using a Hamamatsu Photonics temporal analysis computer system.

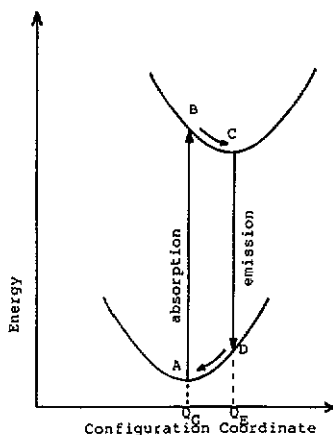


Figure 1. Schematic configuration coordinate diagram illustrating the optical-pumping cycle of a defect centre in solids: A, normal (relaxed) ground state; B, unrelaxed excited state; C, relaxed excited state; D, unrelaxed ground state. Such a configuration coordinate diagram is characteristic for a regular absorption-luminescence cycle without changing the lattice coordinates during the optical transition between the states.

Two emission bands are observed after optical excitation: one has a peak near 512 nm; the other has a peak at 446 nm. Figure 2 shows a typical emission spectrum which was obtained at 40 K. The 512 nm emission band is attributable to the  $A_{T_2}$  emission (Kamishina *et al* 1980). This emission is produced by excitation on the high-energy side of band A (Fukuda 1970a, Kamishina *et al* 1980). The high-energy tail of absorption band A extends up to around 337.1 nm. Therefore the  $A_{T_2}$  emission was produced in addition to the 446 nm emission band B. Here we are concerned with emission band B only. The intensity of the 446 nm emission is almost constant between 15 and 40 K, but it decreases quickly above 90 K with increasing temperature, as shown in figure 3. The 446 nm emission is too weak to be observed at high temperatures above 130 K. Figure 3 shows the temperature dependence of the lifetime of the 446 nm emission band. The 446 nm emission has a lifetime of 27.4 ns at 15 K. The lifetime is almost constant at low temperatures below 40 K, while it decreases with increasing temperature above 40 K. The lifetime  $\tau$  decreases according the usual formula, which is characteristic for a non-radiative transition through an energy barrier of height  $E_a$ :

$$\tau(T)^{-1} = \tau_r^{-1} + \tau_{nr}^{-1} \exp(-E_a/kT) \quad (1)$$

where  $\tau_r$  is the radiative lifetime,  $\tau_{nr}$  the non-radiative lifetime and  $E_a$  the activation energy. The best fit of the observed data to equation (1) was obtained by choosing  $\tau_r = 27.7$  ns,  $\tau_{nr} = 27.2$  ps and  $E_a = 452$  cm $^{-1}$ .

The observed temperature dependence of the emission intensity  $I(T)$  is quite similar to that of the lifetime  $\tau(T)$  as seen in figure 3. The proportionality of the decay rate of the 446 nm emission to the intensity indicates that the drastic change in the decay of emission B is due to the radiationless process from the relaxed excited state of state B to state A (Le Si Dang *et al* 1982).

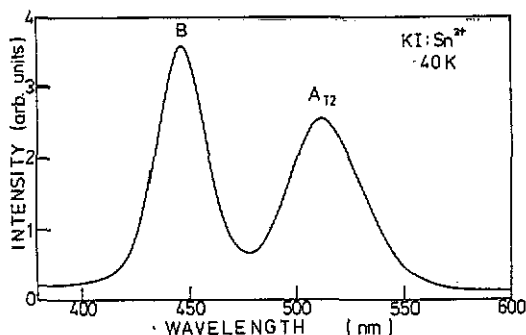


Figure 2. Time-resolved luminescence spectrum of  $\text{KI:Sn}^{2+}$  measured for 10 ns after  $\text{N}_2$  laser pulse excitation at 40 K.

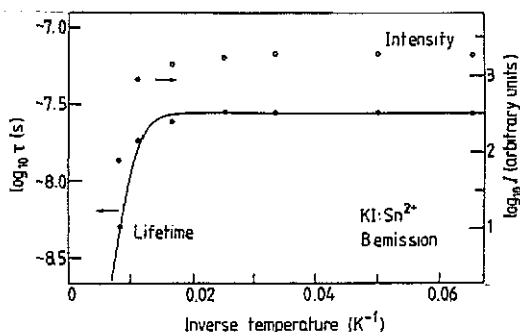


Figure 3. Temperature dependence of the lifetime ( $\bullet$ ) (left-hand scale) and intensity ( $\circ$ ) (right-hand scale) of the 446 nm emission: —, curve obtained with equation (1) from the best fit to the experimental data (see text).

### 3. Discussion

Like the case of the emission B observed for  $\text{KI:Tl}^+$  (Illingworth 1964), the 446 nm emission of  $\text{KI:Sn}^{2+}$  appears only at low temperatures and disappears with increasing temperature. The emission B of  $\text{KI:Tl}^+$  has a lifetime of 1–2  $\mu\text{s}$  (Illingworth 1964). The lifetime is of the same order of magnitude as the lifetime of another forbidden state  $^3\text{P}_0$ ; therefore Illingworth (1964) confirmed that not only absorption band B but also emission band B is characteristic of the 'forbidden' transition. However, the lifetime of the 446 nm emission of  $\text{KI:Sn}^{2+}$  is considerably shorter than that of  $\text{KI:Tl}^+$ . The emission A and emission C for  $\text{KI:Tl}^+$  which are caused by the dipole-allowed transition have a short lifetime of 25 ns (Benci *et al* 1976). The lifetime of 27.4 ns obtained for the 446 nm emission is close to the value of 25 ns, which is the lifetime of the emission caused by the allowed transition. Why is such an extraordinarily fast decay possible for the emission B in  $\text{KI:Sn}^{2+}$ ?

A positive-ion vacancy is located near divalent ions such as  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$  because of charge compensation. The vacancy effect has been confirmed from the lifetime of emission A in  $\text{Sn}^{2+}$ -doped KI and KBr and  $\text{Pb}^{2+}$ -doped KI (Kamishina *et al* 1980, Jacobs 1991, Le Si Dang *et al* 1982, Kang *et al* 1983). the vacancy reduces the symmetry around the  $\text{Sn}^{2+}$  ion in the cubic alkali-halide lattice. This gives rise to a splitting of the excited  $^3\text{P}_2$  states of band B and a mixing of the allowed  $^1\text{P}_1$  state

with the forbidden  $^3P_2$  state. Therefore the wavefunction of the unrelaxed excited state of the  $^3P_2$  state is mixed by the  $^3P_1$  and  $^1P_1$  wavefunctions. The mixing in the unrelaxed excited state is weak, but not so much that the transition is fully allowed, and the absorption band has the character of the 'forbidden' band since the mixing coefficient depends on the coupling to the lattice vibrations. This leads to the formation of the vibration-assisted (and therefore temperature-sensitive) absorption band B. During the electron relaxation process from the unrelaxed excited state into the relaxed excited state, the lattice and vacancy oscillate with large amplitudes towards a new equilibrium configuration because the electron is strongly coupled to the motion of the surrounding ions. As a consequence, after relaxation, the vacancy is displaced to reduce the symmetry around  $\text{Sn}^{2+}$  ions; the geometrical structure around  $\text{Sn}^{2+}$  ions in the relaxed excited state is different from that in the unrelaxed excited state just as in the case of the  $F_A(\text{II})$  centre (Luty 1968), and the symmetry in the former is lower than that in the latter. The lower the symmetry, the stronger is the mixing of the  $^3P_2$  and  $^1P_1$  states. Such a strong mixing with the allowed  $^1P_1$  state leads to an allowed-transition-like luminescence for emission B. In this way, we can understand that the originally forbidden emission B has an extraordinarily short lifetime of 27.4 ns in  $\text{KI:Sn}^{2+}$ .

Unlike the case of the  $F_A(\text{II})$  centre, it is difficult at this moment to clarify how different the vacancy positions are in the relaxed and unrelaxed excited states. Our suggestion that the vacancy moves is consistent with the results obtained by Kamishina *et al* (1980) and Zazubovich *et al* (1987) who studied the emission A, the lifetime and the polarization in  $\text{KCl:Sn}^{2+}$ ,  $\text{KBr:Sn}^{2+}$  and  $\text{KI:Sn}^{2+}$ .

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