

## ENERGY BARRIER BETWEEN SELFTRAPPED AND DELOCALIZED EXCITON STATES IN QUASI ONE-DIMENSIONAL TETRACYANOPLATINATES(II)

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Abstract - Single crystals of  $M[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$  (with  $M = \text{Na}_2, \text{Ba}, \text{KLi}, \dots$ ) are highly anisotropic. In these compounds two different types of excitations are observed: localized selftrapped and delocalized exciton states. From the temperature dependence of the polarized emission of  $\text{KLi}[\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  the height of an energy barrier between the free and the selftrapped exciton states can be estimated. This barrier is responsible for an activated relaxation into the selftrapped states.

Compounds of the chemical constitution  $M[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$  (= MCP) crystallize in columnar structures in which the square planar  $[\text{Pt}(\text{CN})_4]^{2-}$  complexes are arranged parallel to each other. The Pt-Pt separations  $R$  in direction of the stacks are short [ $R(\text{KLiCP}) = 3.20 \text{ \AA}$ ] compared to the distances between the stacks ( $\approx 10 \text{ \AA}$ ). [1] This structure type leads to highly anisotropic electronic properties with a strong electronic interaction in the direction of the stacks (c-axis). By this interaction the lowest electronic transitions are red-shifted by several  $10^4 \text{ cm}^{-1}$  compared to the energies found for dissolved compounds. Thus, the dominant transitions in the solid state occur in the optical energy range and therefore, important information about the properties of the systems can be gained by measuring the (polarized) absorption, reflection, and emission. Since the transition energies strongly depend on  $R$ , which can be varied by cation (M) substitution,

changing the water content ( $n$ ), and/or by application of high pressure, the emission energies, for example, can be tuned from  $26800 \text{ cm}^{-1}$  ( $R = 3.67 \text{ \AA}$ ) to about  $11000 \text{ cm}^{-1}$  ( $R \approx 2.95 \text{ \AA}$ ). [2,3]

Mainly the emission behavior has been investigated in detail to characterize the lowest excited states. These exhibit very different properties:

(1) The *high energetic  $\vec{E} \parallel \vec{c}$ -polarized emission* (component A;  $\vec{E}$  = electric field vector) has a very short lifetime ( $< 0.3 \text{ ns}$ ) and is correlated to a strong  $\vec{E} \parallel \vec{c}$ -absorption (oscillator strength order of one). The corresponding states are ascribed to *delocalized, free exciton* states. This assignment is supported by doping experiments [5] and photoconductivity measurements [4]. (The onset of the photoconductivity is found to lie for BaCP  $\approx 4000 \text{ cm}^{-1}$  above the strong  $\vec{E} \parallel \vec{c}$  transition.)

(2) The *low-energetic emission* (component B) is mainly  *$\vec{E} \perp \vec{c}$ -polarized* and has a low-temperature lifetime of several milliseconds. This emission and the  $\vec{E} \perp \vec{c}$ -absorption are not directly correlated to each other. The component B (but not A) exhibits drastic magnetic field effects, and shows a different pressure dependence compared to component A. Further, energy transfer investigations indicate a localization of the states corresponding to the B-emission to only a few  $[\text{Pt}(\text{CN})_4]^{2-}$  complexes. [5-6] All these properties are consistently explained by the occurrence of *intrinsically localized, selftrapped exciton* states. [2]

The described behavior of the lowest excited states of the tetracyanoplatinates(II) can be ruled back to properties of the hybridized  $\text{Pt}5d_{z^2,6s}$  (HOMOs) and  $\text{Pt}6p_z\text{CN}\pi^*$  (LUMOs) molecular orbitals which strongly overlap for adjacent  $[\text{Pt}(\text{CN})_4]^{2-}$  complexes. (The z-axis of the complexes is parallel or approximately parallel to the c-axis.) A calculation within a tight-binding model using the semi-empirical extended Hückel method leads to band widths of some  $10^4 \text{ cm}^{-1}$  for the valence and the conduction bands. [7] Taking further into account the effects of the electron-hole and the electron-phonon interaction [8] within a highly anisotropic continuum model [9] one finds two types of energy minima in the excited state. The energetically higher lying minimum represents the delocalized free exciton and the lower one the selftrapped exciton, both separated by an energy barrier.

It is subject of this paper to describe the temperature dependence of the differently polarized emissions (components A and B) for KLiCP, as a typical example. [10] Figure 1 shows the spectra at different temperatures and Figure 2 reproduces the intensity ratio  $I(B)/I(A)$ . It increases from  $\approx 5 \text{ K}$  to  $\approx 75 \text{ K}$  by a factor of about 10 and from  $\approx 75 \text{ K}$  to  $300 \text{ K}$  it decreases by a factor of about 35. This behavior can be interpreted by the existence of an energy barrier between the energeti-

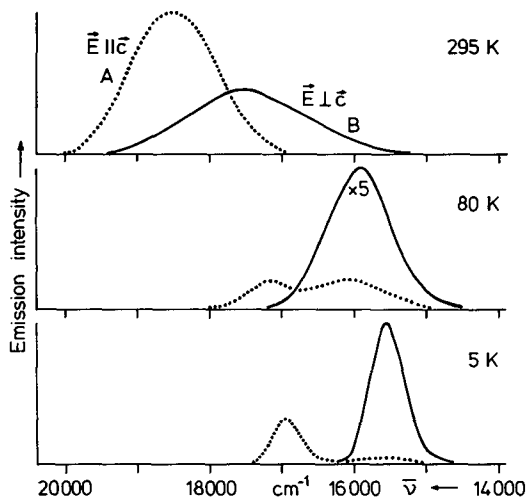


Figure 1. Polarized emission of single-crystal  $\text{KLi}[\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  for different temperatures. Note that at 80 K the  $\vec{E} \perp \vec{c}$ -polarized emission intensity has to be multiplied by a factor of 5 to be comparable to the  $\vec{E} \parallel \vec{c}$ -component. Excitation: 457.9 nm ( $\vec{E} \parallel \vec{c}$ ). For further experimental details see ref.[10].

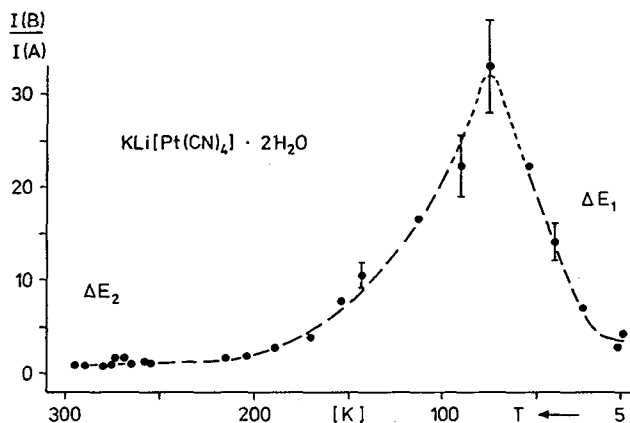


Figure 2. Intensity ratio of the emission components  $I(B)/I(A)$  for single-crystal  $\text{KLi}[\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  versus temperature.[10b] Component A and B represent the high energetic  $\vec{E} \parallel \vec{c}$ - and low energetic  $\vec{E} \perp \vec{c}$ -emission, respectively.

cally higher lying free exciton state and the lower lying selftrapped exciton state. (Fig. 3 illustrates the energetical sequence of the lowest excited states.) At low temperature one finds a spontaneous  $\vec{E} \parallel \vec{c}$ -emission from the free exciton state (component A). With temperature increase from 5 K the barrier can be surmounted which leads to a decrease of the intensity of component A by an activated relaxation process. From the intensity ratio in the low temperature range, presented in Figure 2, the activation energy is estimated to  $\Delta E_1 \approx 30 \text{ cm}^{-1}$  for KLiCP. With further temperature increase above  $\approx 75 \text{ K}$  the relative A-intensity goes up again, which is explained by a repopulation of the free exciton state from the long-living selftrapped state. Thus, the A-emission consists of two components, the short-living spontaneous one and the long-living repopulated component, both exhibiting compa-

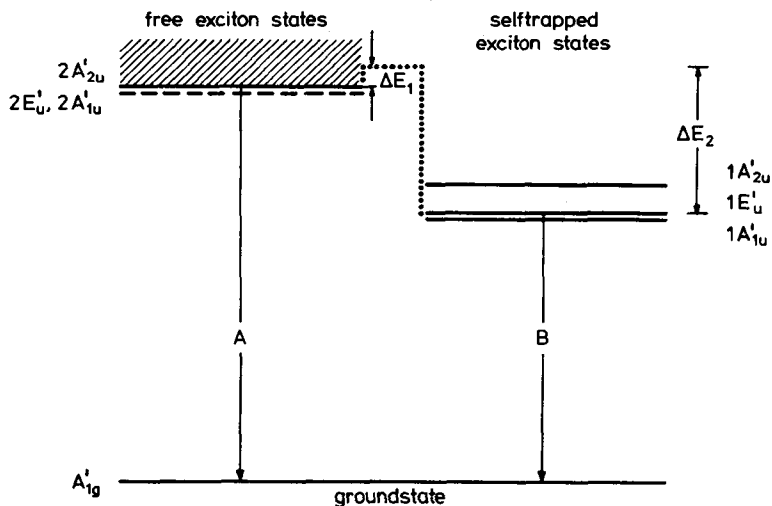


Figure 3.

Schematic and simplified energy level diagram for the lowest excited states of the tetracyanoplatinates(II).[2] The grouptheoretical classification is given for the  $D_{4h}$  symmetry group. The classification of the different selftrapped states results mainly from investigations under high magnetic fields at low temperatures.[11]

rable intensities in the medium temperature range. However, above  $\approx 250$  K the repopulation and thus the delayed emission predominates strongly. Therefore, one can determine the activation energy from the selftrapped to the free exciton state by a simple Arrhenius plot for the high temperature range (Fig. 2). For KLiCP it results  $\Delta E_2 = 1050 \text{ cm}^{-1}$  ( $\pm 15\%$ ).

The activation energies are not independent of the in-chain Pt-Pt distance  $R$ . Further data for  $\Delta E_1$  are not yet available but  $\Delta E_2$  has been determined to  $620 \text{ cm}^{-1}$  (MgCP,  $R = 3.15 \text{ \AA}$ ),  $1470 \text{ cm}^{-1}$  (BaCP,  $R = 3.32 \text{ \AA}$ ), and to  $2700 \text{ cm}^{-1}$  (NaCP,  $R = 3.67 \text{ \AA}$ ).[2]

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