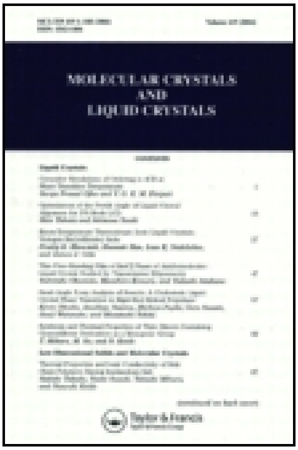

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Transition of Excited States of a Pyrene Single Crystal

Masao Tomura [a], Tadaoki Mitani [b] & Masaaki Tomura [b]

[a] Takeshirodai 4-6-2, Sakai, 590-01, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Masao Tomura , Tadaoki Mitani & Masaaki Tomura (1992): Phase Transition of Excited States of a Pyrene Single Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 67-72

To link to this article: http://dx.doi.org/10.1080/10587259208047017

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 67–72
Reprints available directly from the publisher
Photocopying permitted by license only

PHASE TRANSITION OF EXCITED STATES OF A PYRENE SINGLE CRYSTAL

MASAO TOMURA, TADAOKI MITANI* and MASAAKI TOMURA*
Takeshirodai 4-6-2, Sakai 590-01, Japan
*Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract Luminescence decay time and quantum yield of a pyrene single crystal are observed by a pulse method between 40-300 k. The temperature dependence on the intrinsic life time of emissions shows a peculiar character. The abrupt change of the analyzed intrinsic life time corresponds to the critical temperature of the phase transition. The mechanism of the phase transition is attributed to the formation of the trapped excimer excitons which deform the lattice around them. Further, the phase transition is concluded as the first kind type.

INTRODUCTION

There were many studies of phase transitions of magnetic, dielectric, and organic substances. However, they were carried out for ground states. The phase transition of pyrene was studied about specific heat, X-ray structure, and optical transmission characters for only the ground state.

The present work is studied about the phase transition for the excited state between 40-300 K, and the mechanism of the phase transition is discussed.

EXPERIMENTAL

A single crystal of pyrene was grown by a vapour transport method. The flake crystal was about 0.5 × 0.5 × 5×10^{-4} cm^3 in size. The specimen was irradiated by a N_2 pumped dye laser at 380 nm in perpendicular to the face of the flake. The pulse width was about 7 ns. The irradiation power onto the specimen was about 1.3 mJ/pulse. Luminescence was observed at 470 nm with a boxcar integrated signal averrager. One example of the emission decay curve is shown in Figure 1. The decay curve is of single exponential type with time constant τ and its temperature dependence is shown in Figure 2a. The quantum yield η of the emission was observed only relatively. However, real values of η are estimated to fit Eq. (2) by taking suitable q_i values mentioned afterwards, according to the work[1] for powder pyrene, and shown in Figure 2b.

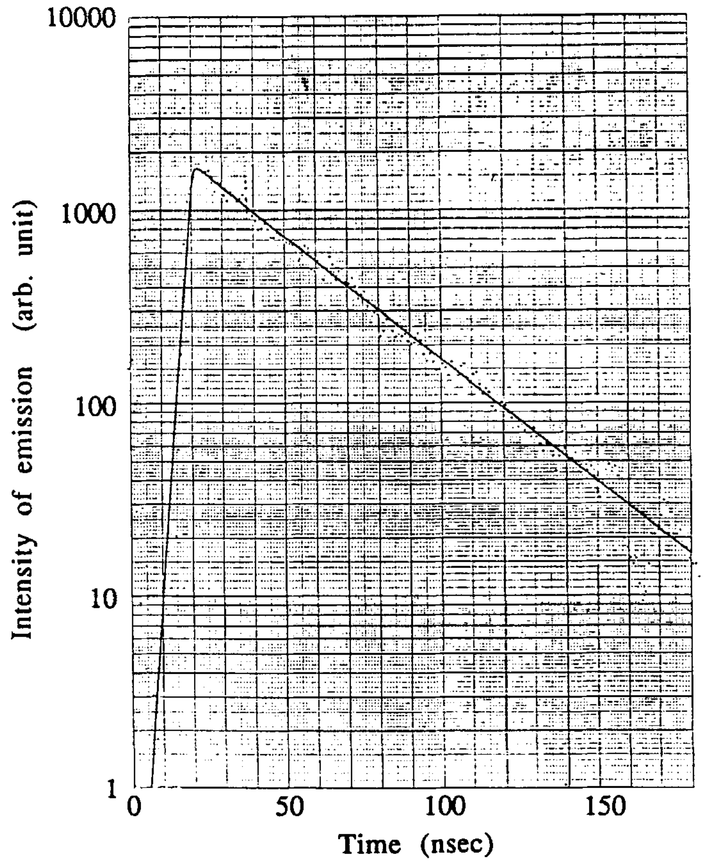

FIGURE 1 Decay curve of an emission at 225.5 K.

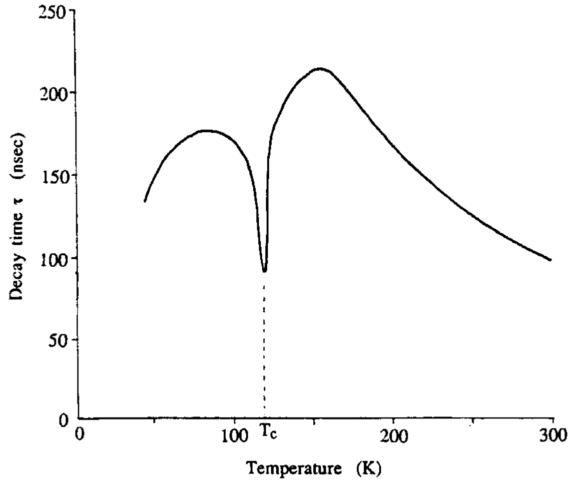

FIGURE 2a Temperature dependence of the emission decay time τ.

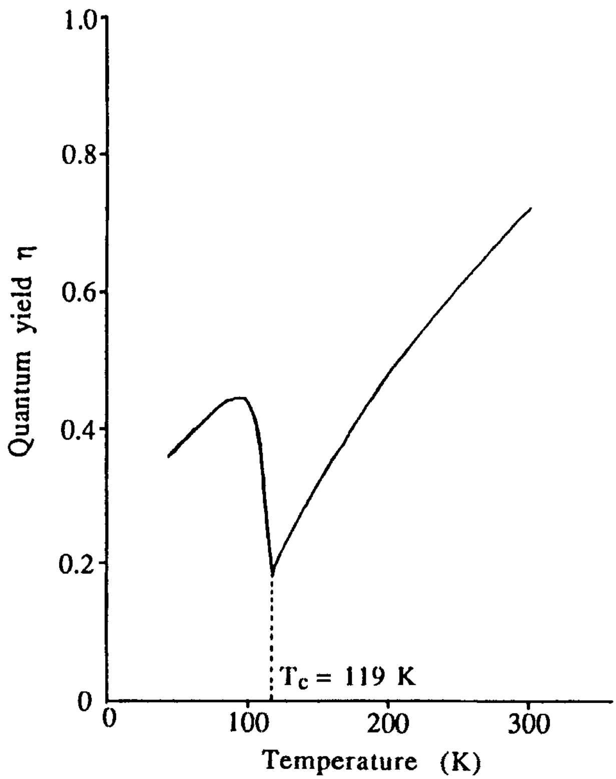

FIGURE 2b Temperature dependence of quantum yield η of the emission.

RESULTS

The pyrene emission is considered as the decay processes from free excimer excitons and two kinds of trapped excimers A and B.[2,3] The corresponding these excimer states are schematically shown in Figure 3.

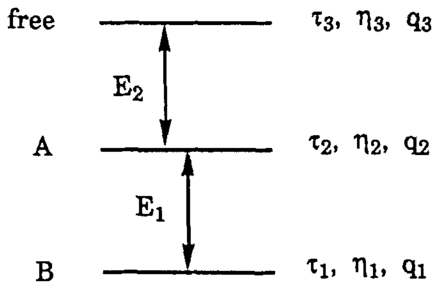

FIGURE 3 Excited states of a pyrene crystal.

Where E_1 and E_2 are energy differences between the A and B states; and between the free and A states, respectively. The τ_i, η_i, and q_i are life time, emission yield, and thermal quenching rate of each i th state, respectively.

Since observed decay curves are of the single exponential type, quasi-thermal equilibrium is established among the excited population of the three states before the emission process. In this case, observed τ and η are given by following Eq. (1) and (2), respectively.

$$\tau = \frac{1 + e^{-\frac{E_1}{kT}} + e^{-\frac{(E_1+E_2)}{kT}}}{\left(\frac{1}{\tau_1} + q_1\right) + \left(\frac{1}{\tau_2} + q_2\right) e^{-\frac{E_1}{kT}} + \left(\frac{1}{\tau_3} + q_3\right) e^{-\frac{(E_1+E_2)}{kT}}} \qquad (1)$$

$$\eta = \frac{\frac{1}{\tau_1} + \frac{1}{\tau_2} e^{-\frac{E_1}{kT}} + \frac{1}{\tau_3} e^{-\frac{(E_1+E_2)}{kT}}}{\left(\frac{1}{\tau_1} + q_1\right) + \left(\frac{1}{\tau_2} + q_2\right) e^{-\frac{E_1}{kT}} + \left(\frac{1}{\tau_3} + q_3\right) e^{-\frac{(E_1+E_2)}{kT}}} \qquad (2)$$

The intrinsic life time τ_0 is given as τ/η, therefore, Eq. (3) is obtained.

$$\tau_0 = \frac{1 + e^{-\frac{E_1}{kT}} + e^{-\frac{(E_1+E_2)}{kT}}}{\frac{1}{\tau_1} + \frac{1}{\tau_2} e^{-\frac{E_1}{kT}} + \frac{1}{\tau_3} e^{-\frac{(E_1+E_2)}{kT}}} \qquad (3)$$

Then, the temperature dependence of τ_0 is shown in Figure 4. From the temperature dependence of τ_0, the fitting parameters E_1, E_2, τ_1, τ_2, and τ_3 can be determined. They are written in the figure only above T_c.

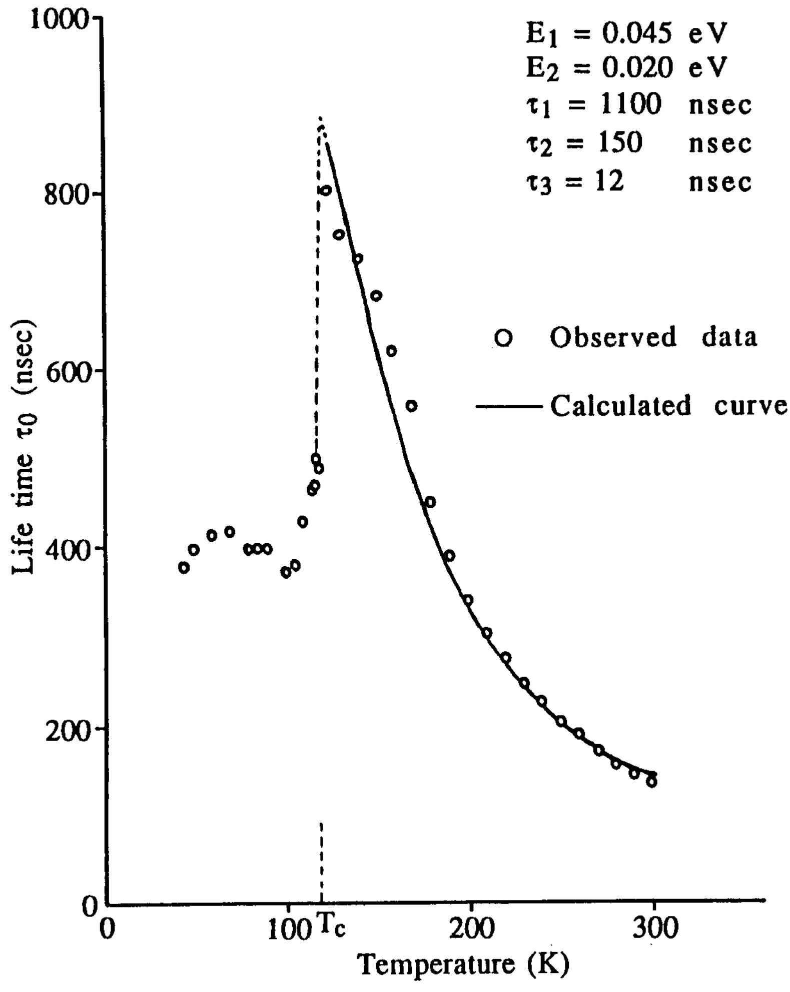

FIGURE 4 Temperature dependence of the emission life time τ_0.

The phenomenon of the very sharp change of τ_0 at T_c in the figure is corresponds to the phase transition of the pyrene crystal. These clear transition behavior at T_c has not been observed in experiments of the phase transitions for the ground state. Below T_c, another temperature dependent τ_0 curve is observed as shown in Figure 4. This means the change of the structure of the lattice below T_c, and an appearance of other type of three excimer states.

Though the shape of τ_0 curve around T_c is peculiar, the type of the phase transition is considered to be the first kind. The reason of the peculiar shape above T_c is due to the existence of three excimer states and their character in the quasi-thermal equilibrium.

The number of incident laser photon is estimated about 4×10^{16} photons/pulse and the number of the molecules in the irradiated part of the specimen is 8×10^{15}, therefore all of the pyrene molecules are excited. Then excimers are produced in the all molecules. At T_c excited excimers populate only the lowest state B, occurring the phase transition as seen in Figure 4. This result indicates only the B trapped excimer deforms lattice[4] around them, leading the phase transition. According to A. Matsui[5], in the case of no irradiation of light the phase transition does not occur until 4 K. This fact supports the result mentioned above.

REFERENCES

1. Y. Takahashi, T. Kitamura, K. Uchida, and M. Tomura, J. Luminescence, 21, 269 (1980).
2. M. Tomura and Y. Takahashi, J. Phys. Soc. Japan, 31, 797 (1988).
3. R. Seyfang, H. Port, and H. C. Wolf, J. Luminescence, 42, 127 (1980).
4. W. Jones, S. Ramdas, and J. M. Thomas, Chem. Phys. Letters, 54, 490 (1978).
5. A. Matsui, Private Communication.