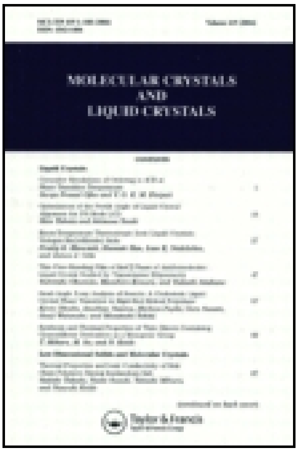

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Behaviour of the Energy States of Defects in Phenanthrene Crystals in the Region of a Phase Transition

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The regularities of thermostimulated processes in a phenanthrene crystal at its phase transition temperatures have been studied by thermoactivated spectroscopy. A phenomenological model describing the changes in the energy spectrum of crystal local states in the vicinity of a phase transition has been proposed.

1. INTRODUCTION

Structural phase transitions (PT) in molecular crystals may markedly affect the electronic structure of a crystal[1] leading to the changes in the mobility of charge carriers,[1] photoconductivity[2] electrical conductivity[1,2] and other characteristics. However, the behaviour of the local levels of the defects in the vicinity of PT for organic systems has not practically been investigated.

One of the efficient methods to study the local states for charge carriers in organic substances proved to be thermostimulated luminescence (TSL) (see References 3–8). This method has been used to study PT of the melting or glass-transition types[3,6,8] in organic crystals and polymers. It has been established[3] that in the cases of PT the kinetics of a thermostimulated process cannot be described by the known Arrhenius relationship. Instead the empiric equation used for the description of the viscosity at temperatures of glass phase transition has been proposed for glass PT in amorphous polymers.[3] This approach has presumably been substantiated insufficiently. Also it has turned out to be invalid for other structural PT. Thus no satisfactory model is available for the description of thermostimulated processes in PT regions.

It is known that a structural PT with an orientationally disordered phase at $T > T_c$ occurs in a phenanthrene crystal ($C_{14}H_{10}$) at $T_c = 345$ K, which has been observed in X-ray studies[9] and during positron annihilation.[10] It has also manifested itself in abnormal temperature-dependent electric conductivity,[2] permittivity,[9,11] pyroelectric,[9] optical,[9,12] acoustic[9] characteristic of the crystal.

The nature of such a PT has not yet fully been elucidated. PT in phenanthrene was suggested to be probably pseudoproper ferroelectric.[9] It has not yet been studied by thermoactivated spectroscopy.

The present paper deals with the behaviour of the energy spectrum of local states in a phenanthrene crystal in the region of PT studied by the TSL method.

2. EXPERIMENTAL AND EXPERIMENTAL DATA TREATMENT

Phenanthrene was purified by zone melting (more than 100 zones). The phenanthrene monocrystals grown by the Bridgman method, as well as phenanthrene polycrystals were investigated. Two independent types of experiments were carried out.

a) The temperature-dependent intensity of TSL $I(T)$ was measured over the temperature range 4.2–370 K. To obtain the thermoluminescence glow curves (GC) the samples after illumination with mercury lamp light were heated at a constant rate of 0.1 K/s. In some cases crystals were preliminary annealed in darkness. The accuracy of registration of the sample temperature was $\Delta T < 0.1$ K. In the case of first-order kinetics, the intensity of TSL is determined by the expression[3]:

$$I(T) = I_o \times \exp(-E_a/kT) \times \exp(-S/\beta \times \int_{T_o}^{T} \exp(-E_a/kT')dT'), \quad (1)$$

where activation barrier magnitude, E_a, and the frequency factor, S, are independent of temperature; k is the Boltzman constant; $\beta = dT/dt$ is the rate of heating.

We believe that in the case of PT in phenanthrene this condition has not been fulfilled. Therefore, a more general case taking into account the dependence of activiation energy on temperature in the vicinity of PT should be considered using relationship (1). In this satuation and assuming a monoenergetic level of the traps, we determine $E_a(T)$ by the formula:

$$E_a(T) = k \times T \times \ln\left[(I_o - \frac{S}{\beta} \times \int_{T_o}^{T} I(T')dT')/I(T)\right]. \quad (2)$$

b) The energy spectrum of the traps of charge carriers was determined by the fractional glow technique[14] which uses multiple periodicity of a "heating-cooling" cycle of the sample. The effective activation energy, E_{eff}, is obtained with the help of the relationship[14]:

$$E_{\mathrm{eff}} = -\frac{d \ln I}{d(1/kT)}. \quad (3)$$

The mean temperature, T, was assigned to each temperature range in which E_{eff} was estimated. The periodicity of changes in E_{eff} over the temperature range 315–340 K was found to be 1 K.

Since the activation barrier E_a in thermoactivation processes remains constant or slightly changes, the experimentally measured $E_{\text{eff}} = E_a$. In the cases when such a condition is not valid, $E_a(T)$ may be also obtained from the experimental $E_{\text{eff}}(T)$ solving the equation derived from (1) and (3):

$$\frac{dE_a}{dT} - \frac{E_a}{T} - \frac{S}{\beta} kT \times \exp(-E_a/kT) = -\frac{E_{\text{eff}}}{T}. \tag{4}$$

In this temperature range the frequency factor, S, was chosen to correlate the results in $E_a(T)$ derived from the experimental data. E_{eff} at $T = 310$ K when changes in E_a may be neglected were used as the initial condition.

It should be noted that relationship (1) used for analysis of experimental data actually involves $S \times (-E_a/kT)$ which makes it impossible to distinguish between the E_a and S temperature dependences. We believe that the observed effects arise due to the temperature-dependent activation energy in the vicinity of PT, rather than to a frequency factor, S. This assumption is confirmed by a decrease in the activation energy of electric conductivity of a phenanthrene crystal after PT from 1.5 to 1.1 eV.[2] Since the forbidden energy gap of this crystal is 4.9 eV, intrinsic electric conductivity presumably manifests itself and the change in the activation energy of the latter points out to the change in the depth of localized levels at PT in the crystal.

3. RESULTS

The glow curves for phenanthrene crystals over the temperature range 4.2–300 K are a set of overlapping bands with maxima at 100–200 K which agrees with the TSL data[4–5] for these crystals. The effective activation energies measured in this region are also consistent with the data published in Reference 5.

While studying the phenanthrene monocrystals grown up by the Bridgman technique, using the TSL method we have revealed a new high-temperature glow peak with the maximum at $T = 338$ K (Figure 1, Curve 1).

After preliminary heating of the virgin phenanthrene crystals up to c.a. 350 K and the subsequent rapid cooling up to the temperature below PT, the intensity of the high-temperature peak in the glow curve drops practically to zero (Figure 1, Curve 2).

In this case the low-temperature TSL bands appreciably shift to lower temperatures. At the same time the intensity of this peak is nearly fully resumed upon slow cooling of the crystal from 360 to 300 K at a rate of approximately 1 K/h or its staying at room temperature for a month. Such a peak was not observed in the polycrystals grown up from the melt.

It should be noted that there exists a correlation in the behaviour of TSL and permittivity ε within the region of PT temperature consisting in the following: TSL in this region, as well as a sharp anomaly $\varepsilon(T)$[9] are observed only in the first heating cycle and are absent in the subsequent changes. On prolonged storage of crystals at $T = 300$ K the anomaly of $\varepsilon(T)$,[9] and also the TSL peak are resumed.

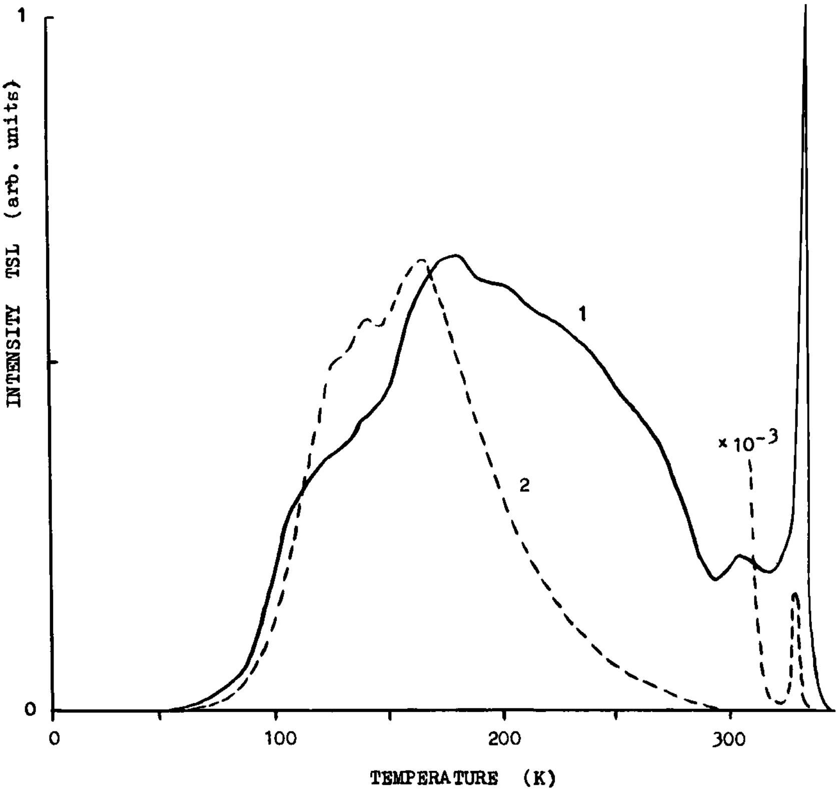

FIGURE 1 A temperature-dependent intensity of the thermostimulated luminescence, I, of a phenanthrene crystal (illumination at $T = 4.2$ K; the heating rate 0.1 K/s for a crystal grown up by the Bridgman method: the virgin crystal—(1) and the preliminary heated in darkness up to $T > 345$ K and then rapidly cooled to $T = 300$ K—(2).

A new high-temperature glow peak for phenanthrene essentially differs from the rest of low-temperature TSL bands of this crystal:

1. It is characterised by an abnormaly small semiwidth ($\Delta T = 5$ K) (Figure 2a).
2. E_{eff} in this region drastically increases with temperature (Figure 2a) and amounts a gigantic magnitude, above 30 eV, i.e., it is fictitious and does not correspond to the activation barrier value;
3. The frequency factor in this region also proves to be abnormally high ($S > 10^{50}$ s^{-1}).

Figure 2 (Curve 3) shows the glow curve calculated according to (1) for a given temperature region using temperature-independent E_a and S values ($E_a = 0.93$ eV, $S = 4.4 \times 10^{11}$ s^{-1}). The experimental glow curve proved to be markedly narrower than the calculated one (Figure 2a). It follows from the above that the thermoactivation process in the phenanthrene crystal in the region of PT cannot be described by the Arrhenius relationship. It is evidently due to the fact that at PT E_a is inconstant and depends on temperature.

In the framework of this assumption we have calculated the temperature-dependent $E_a(T)$ under the initial conditions $E_a(T = 310\text{ K}) = 0.93$ eV using

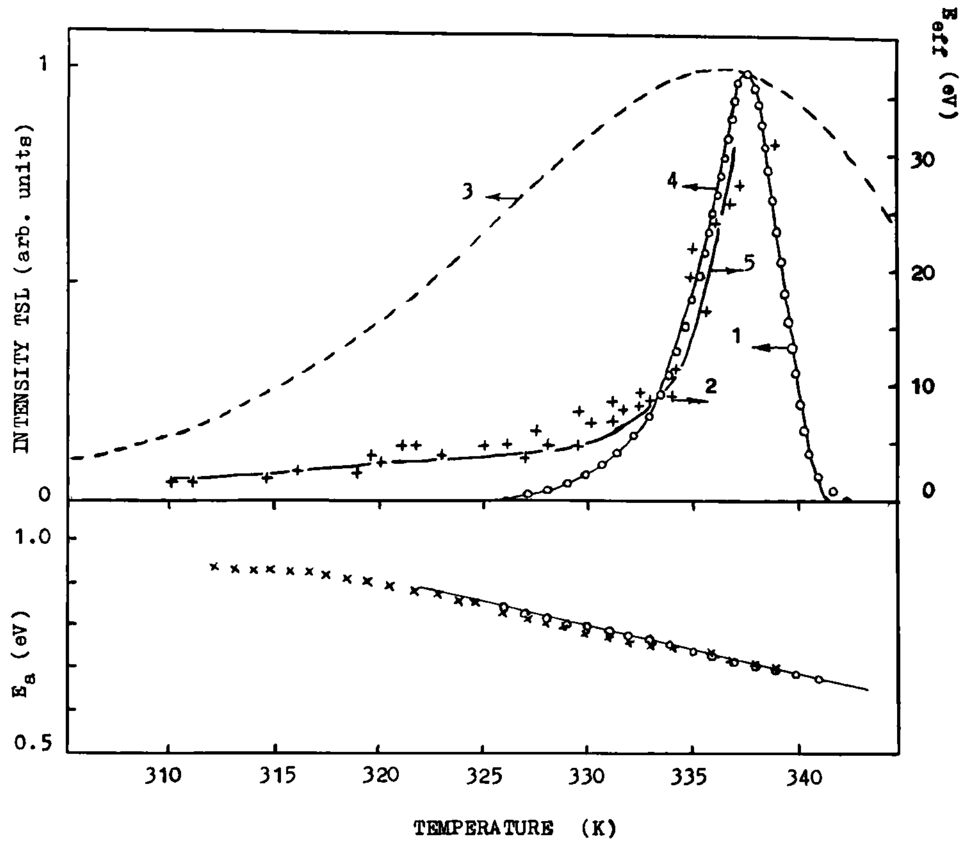

FIGURE 2 The characteristics of a thermoactivated processes at temperatures of structural PT in a phenanthrene crystal: a) Experimental temperature-dependent intensity of TSL, $I(T)$, (light circles) and effective activation energy, E_{eff}, (crosses), as well as these dependences calculated according to (1) and (4) provided that $E_a = E_a(T)$ according to (5) (curves 4 and 5, respectively). For comparison, the thermoluminescence glow curve (curve 3) calculated by (1) when E_a and S ($E_a = 0.93$ eV, $S = 4.4 \times 10^{11}$ s^{-1}), are constant. b) The temperature dependent activation energy, E_a, calculated from the experimental $I(T)$ (light circles) and $E_{eff}(T)$ (crosses) according to (2) and (4), respectively. A solid line stands for the approximation of the data according to (5).

Equations (2) and (4). The results of the calculation of $E_a(T)$ obtained from the experimental $I(T)$ and $E_{eff}(T)$ dependences coincide (Figure 2b). Thus the proposed approach permits one to interpret the basic features of TSL in the vicinity of PT: 1) the glow curve becomes much narrower; 2) the E_{eff} values are considerably higher than the real E_a value and drastically increase at $T \rightarrow T_c$.

It follows from the calculations performed for E_a (Figure 2b) that the trap depth at $T \rightarrow T_c$ decreases according to the linear law:

$$E_a(T) = \overset{o}{E}_a + E' \times (T_c - T), \tag{5}$$

where $\overset{o}{E}_a = 0.63$ eV, $E' = 0.0115$ eV. At temperatures, where TSL was observed, the trap depth decreases by approximately 0.2 eV, which is responsible for the increase in the thermoactivation process and the narrowing in the TSL band. These values may be roughly evaluated using the fact that after heating of crystal up to $T > T_c$ and the subsequent rapid cooling to $T = 300$ K, the low-temperature phenanthrene TSL bands shift to lower-temperatures. It is obvious that this shift accounts for the fact that the decrease in the trap depth resulted from PT retains after such a rapid cooling. We have measured this shift using a phenanthrene crystal doped with tetracene creating a trap with $E_{\mathrm{eff}} = 0.80$ eV. After the above mentioned thermotreatment $E_{\mathrm{eff}} = 0.62$ eV, i.e. it decreased by 0.18 eV (Figure 3).

The suggestion that the activation barrier changes depending on temperature has been used earlier[15–17] to describe thermoactivation processes in the rearrangement of a defect structure not connected with PT in certain ionic crystals. To describe the regularities of TSL in the regions of unfreezing the ionic mobility in a variety of alkali-haloid crystals[16–17] and reorientate depth centres in $LiNbO_3$,[15] the authors have proposed a model assuming the presence of two states (perturbed and unperturbed) with different trap depths and thermoactivation transitions between states. However, in our case such an approach proved to be invalid, since when simulating a glow curve at any physically permissible activation energy of

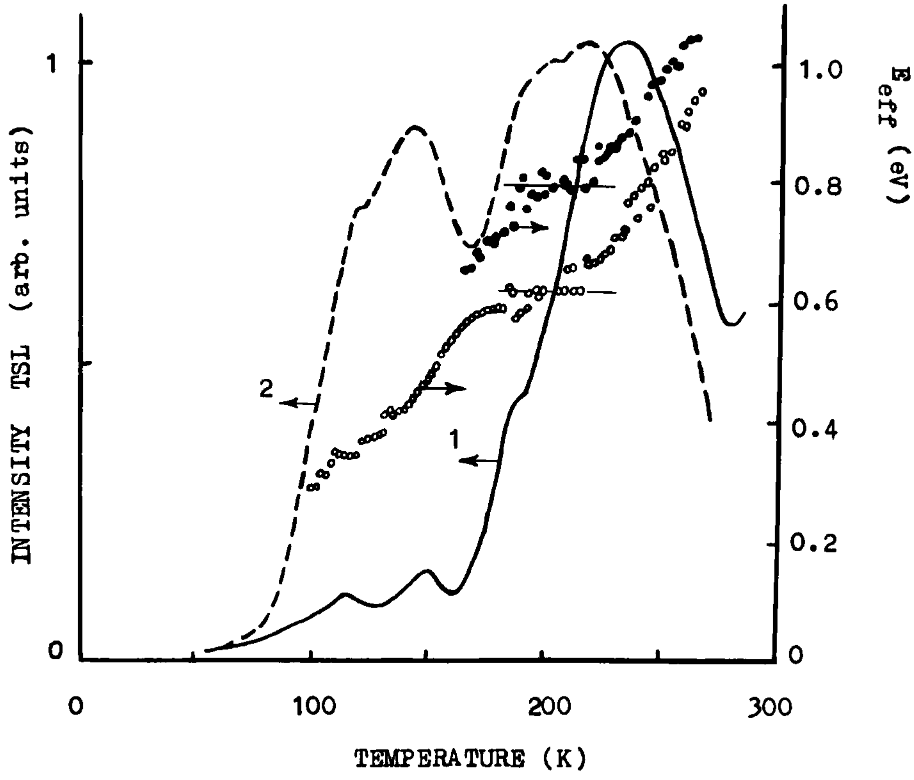

FIGURE 3 Temperature-dependent intensities of TSL $I(T)$ for a phenanthrene crystal doped with tetracene ($C = 0.3\%$) grown up by the Bridgman technique; the virgin crystal—(1) and preliminary annealed to $T > 345$ K and then rapidly cooled to $T = 300$ K—(2); as well as effective activation energies, E_{eff}, in the region of the TSL peak stimulated by tetracene for the virgin and annealed crystals (black and light circles, respectively); the heating rate 0.005 K/s.

structure rearrangement and the corresponding frequency factor we have failed to obtain a curve close to the experimental one with so small semiwidth and such high E_{eff} values.

4. DISCUSSION

This suggestion of the dependence of trap depth as a linear function on temperature at $T \rightarrow T_c$ qualitatively and quantitatively describes the experimental data obtained.

A detailed dependence of local level position on temperature at PT may be established providing the known model of structural rearrangement induced by PT, as well as the nature of charge carrier traps. There is no unambiguous PT model at $T = 345$ K in phenanthrene so far. Therefore, we will describe phenomenologically the behaviour of a temperature-dependent level at $T \rightarrow T_c$ and discuss the possible interpretation of such a behaviour.

We think that the trap depth like other crystal characteristics at $T \rightarrow T_c$ may be described by a function of reduced temperature:

$$E_a = f\left(\frac{T_c - T}{T_c}\right). \tag{6}$$

It follows from the experimental data that at $T \rightarrow T_c$ one can observe a linear temperature behaviour of the contribution of crystalline effects to activation energy (Figure 2b). The depth magnitude (0.93 eV) of the trap indicates its admixture character since the depth of structural traps cannot exceed 0.5 eV.[18] When studying the thermo e.m.f. of phenanthrene crystals at 330–360 K with the electrodes made of silver paste we have established that the conductivity is of a hole nature. The depth of a hole admixture trap is determined by the relation[18]:

$$E_h = \Delta I_g - \Delta P, \tag{7}$$

where ΔI_g is the difference in the ionization potential for crystal and admixture molecules; ΔP is the difference in electronic polarization of the crystal upon the localization of the carrier crystal and admixture molecules.

ΔP may also involve a deformation-induced level shift. Different sizes of the crystal molecules and admixture molecules are responsible for the ΔP value which amounts to 0.1–0.2 eV.[18] ΔI_g characterizes molecules, whereas ΔP is determined by a crystal interaction and may undergo essential changes at PT.[13]

One may propose several models of centres inducing the observed dependence $E_a(T)$. For instance, when charge carriers are entrapped by the admixture, multipole (dipole, quadrupole) moments change which leads to changes in the admixture polarization energy with environment. The polarization energy, depends on permittivity ($P \sim 1 - 1/\varepsilon$), therefore, in cases when the Curie-Weies law ($\varepsilon \sim 1/(T - T_c)$) holds true, in the vicinity of PT $\Delta P \sim (T - T_c)$. It is evidenced from the experimentally observed correlation in the behaviour of TSL and permitivity ε over this temperature range.

The formation of local centres of the "admixture-vacancy" complexes decomposed (induced) at PT is also possible. This assumption is indirectly confirmed by the data on positron annihilation at PT in phenanthrene[10] and may account for the difference in TSL of crystals after rapid or slow cooling at PT temperatures, (Figure 1), as well as a slow regeneration of samples due to annealing at room temperature.

A more unambiguous determination of the model needs further investigations.

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