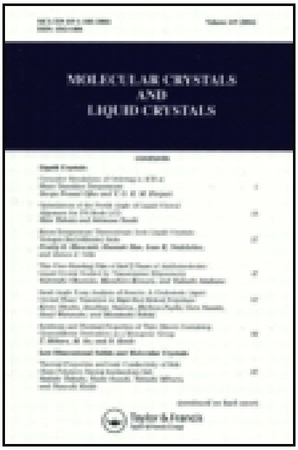

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A Radiothermoluminescence Investigation of Electron Trapping and Recombination in a Supercooled and Crystallized Liquid Crystal†

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The technique of radiothermoluminescence (RTL) has been used to investigate electron trapping and recombination in the mesomorphic compound 4-butoxybenzylidene-4'-hexylaniline (4–6) in both the low temperature supercooled phase and the low temperature crystalline phase, as well as at the higher temperatures of the mesomorphic transitions. The RTL spectra obtained are compared with DSC spectra over the same temperature ranges. From this data, the trapping depths and distributions have been determined, as well as the energy distribution of the recombination centers.

INTRODUCTION

Mesomorphic phases, consisting as they do of oriented molecules, reflect this orientational order in having anisotropic physical and electrical characteristics. Electrical properties, such as electron/hole mobilities, the depth and distribution of trapping levels, the energy location of the recombination centers, as well as their associated capture cross sections, would most likely be influenced by the underlying molecular order.

The technique of radiothermoluminescence (RTL) has recently been added to the list of those techniques which have been successfully uti-

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lized to investigate the electrical characteristics of mesomorphic compounds.[1] In applying this technique to organic compounds in general, a sample, usually held at liquid nitrogen temperature, is irradiated with some form of high energy electromagnetic or particle radiation. This process results in the excitation of large numbers of electrons into the conduction band, some of which fall subsequently into localized trapping sites. Upon heating, the electrons escape from the traps and fall into their ground states, often via an intermediary recombination center. The light emitted during the deexcitation process is monitored with a photomultiplier.

EXPERIMENTAL

The liquid crystal compound 4-butoxybenzylidene-4'-hexylaniline (4–6) was synthesized, recrystallized 4 times in an inert atmosphere utilizing literature techniques[2] and subsequently zone refined for 60 sweeps in which the compound was cycled through the smectic A ↔ nematic phase transition (54°C). This particular compound was chosen because, as shown below, it exhibits 3 distinct phases between the crystalline solid and the isotropic liquid phases. The relatively wide separation of these phase transitions facilitated observation of the effect of the mesomorphic phase changes upon the RTL spectra of the compound.

60 mg samples of the 4–6 compound were prepared and cooled rapidly from the smectic A state by quenching in liquid nitrogen, thereby forming a supercooled smectic phase. Half of these samples were subsequently warmed to 15°C and held at this temperature for 12 hours. An analysis using a differential scanning calorimeter (DSC) showed that these samples had crystallized, whereas those kept in liquid nitrogen exhibited no crystallization.

All the samples were then immersed in liquid nitrogen and irradiated with .5 to 4.5 Mrad of Co^{60} γ-radiation. The samples were then warmed at rates of 5°C to 18°C per minute, the light emitted being monitored with an Oriel photomultiplier and associated 7060 detection system. A typical RTL spectra thus obtained is shown in Figure 1, along with the corresponding DSC, for samples frozen in the supercooled smectic state. Figure 2 shows the comparable RTL and DSC spectra for samples frozen in the crystalline phase. Though the two RTL spectra differ significantly below the 25°C melting point, only one difference between the two DSC spectra is observed. This difference appears most distinctly in the graph in Figure 1 labeled DSC 1–DSC 2 in

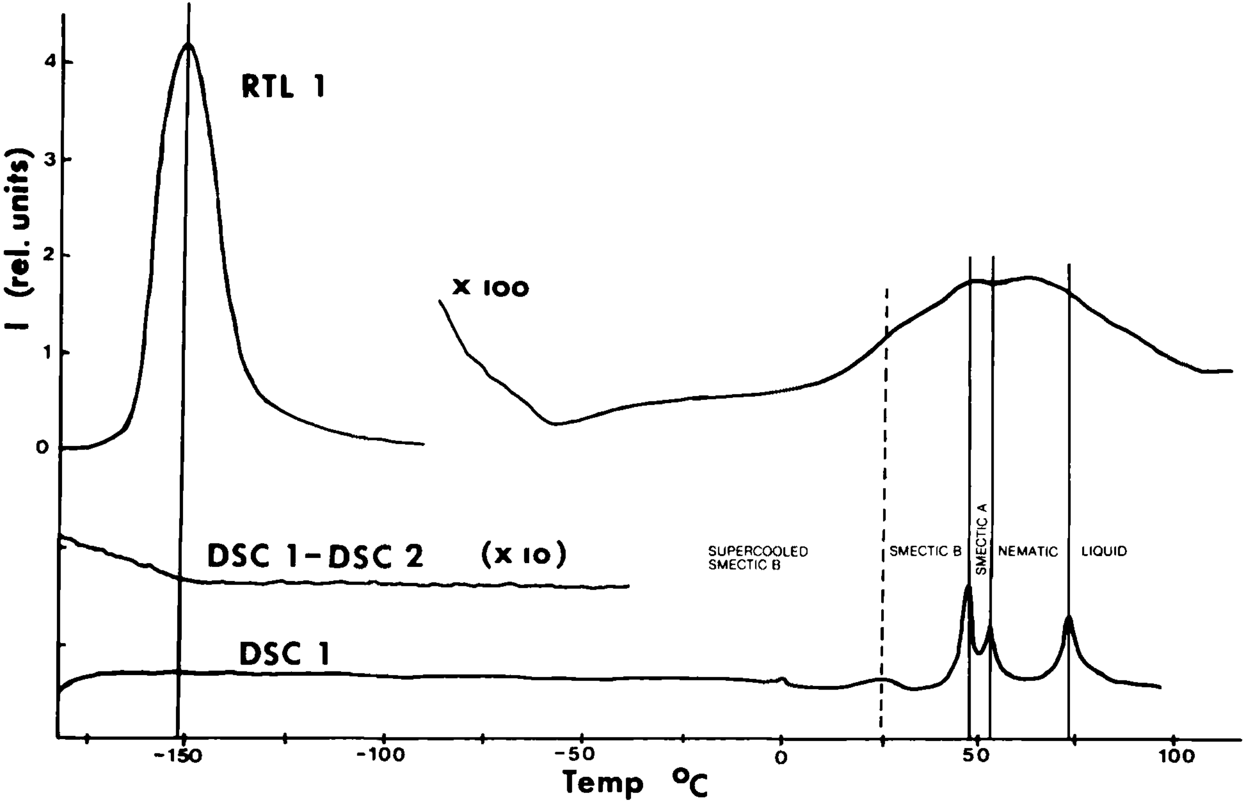

FIGURE 1 RTL glow curve and DSC spectra for supercooled (4–6). Also shown is DSC 1 minus DSC 2. Heating rates are 8°C/min.

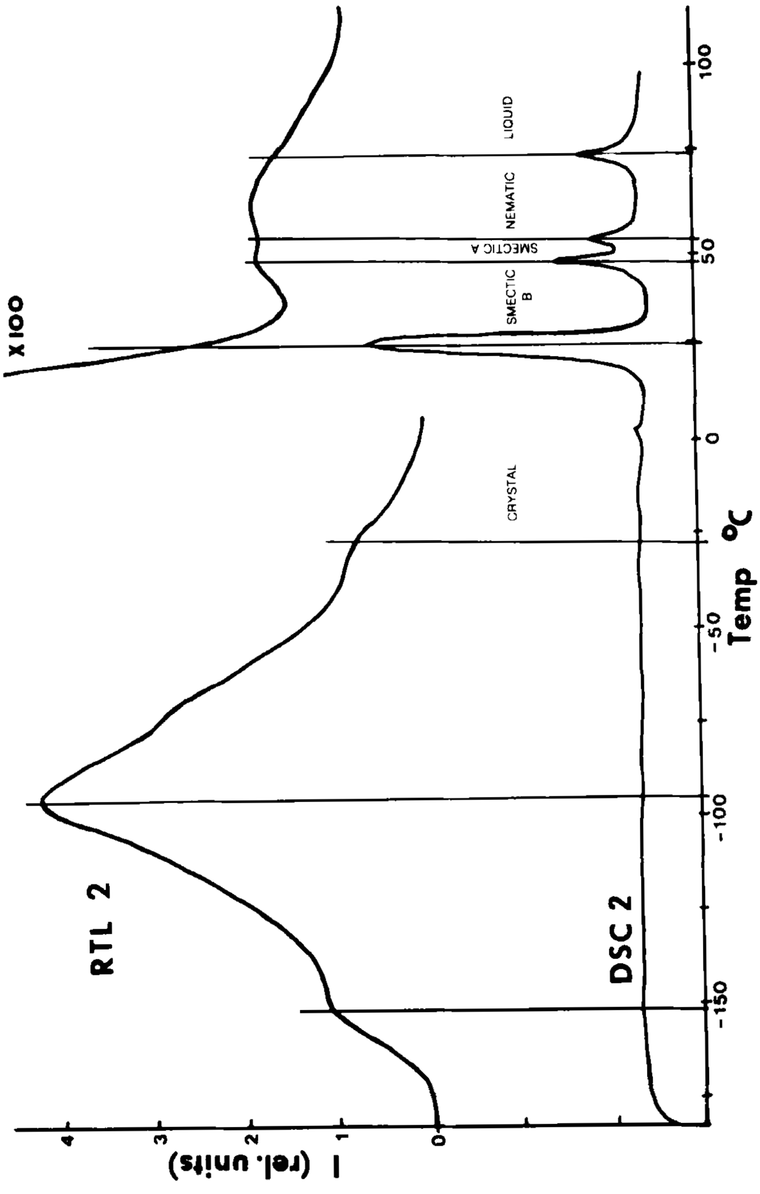

FIGURE 2 RTL glow curve and DSC spectra for crystallized (4–6) at heating rates of 8°C/min.

which a change in slope is clearly observed at −148°C. The single low temperature peak in the RTL spectra of the supercooled sample is centered at −152°C and apparently corresponds to the β transition observed in the region of the glass point (a second order transition) in many polymers.[3] The 4°C difference between the slope change of the DSC and the peak maximum of the RTL peak most likely reflects the different relaxation frequencies associated with the two physical processes. The RTL spectra of the crystallized sample shows a broad peak centered at −92°C overlapping two smaller peaks at −152°C and −27°C. The crystal → smectic B transition, observed in the DSC at 25°C, appears as a sharp drop in the RTL spectra in the crystallized sample. The smectic B → smectic A transition at 48°C corresponds to the first high temperature peak in the RTL spectra, while the smectic A → nematic transition at 54°C occurs 2°C after the minimum between the two high temperature RTL peaks. No RTL structure is observed at the 77°C nematic → isotropic liquid transition.

DOSE KINETICS

If there exist a constant number of trapping sites in each sample, then the glow intensity of a peak is a function of the irradiation dosage, up to some saturation level, at which point virtually all the available traps are filled. Boustead and Cherlesby have shown that the area of the glow peaks can, with the assumption of a constant number of trapping sites, be expressed as: $I = A(1 - e^{-B\sigma r})$, where A is a proportionality constant, B is the dose rate of production of free electrons (of the order of 1.3×10^{17} electrons/Mrad), σ is the electron capture cross section of the trap and r is the total radiation dosage.[4] A least squares fit of the measured integrated light intensity of the single peak from the RTL spectra of the supercooled smectic as a function of the radiation dosage (in 4 intervals, from .3 to 2.3 Mrad), yields an electron trapping cross section for the trap of the order of 1.6×10^{-17} cm^2. The comparable cross section obtained from the crystallized sample is 1.4×10^{-17} cm^2. These values are similar to the effective cross sections observed for traps in many organic and inorganic crystals.[4,5]

It is significant to note that in each case the radiation kinetics do follow a saturation curve of the form of the above dose kinetics equation. If the electron trapping sites resulted from the radiation damage of the sample, rather than being characteristic of the sample and its preparation, then the dose kinetics would be of the form $I \propto r^2$, a relationship which is not here observed.

ELECTRON TRAP ACTIVATION ENERGIES

If the observed luminescence peaks are envisioned as arising from electrons escaping from localized traps of depth *E*, due to the thermal energy kT of the trapped electron, then the observed peaks can be fit to a theoretical kinetics model to yield the single adjustable parameter *E*. If the electron is instead pictured as escaping from the trap due to some fundamental change in the trapping site (e.g. if at a given temperature the portion of the molecule adjacent to the trap gains an additional degree of rotational mobility), then the value of *E* produced by fitting to the model represents the activation energy associated with the filled trap changing process.

Shown in Figure 3 is a typical RTL glow peak obtained from the supercooled smectic sample and the best fit of this data to a first order

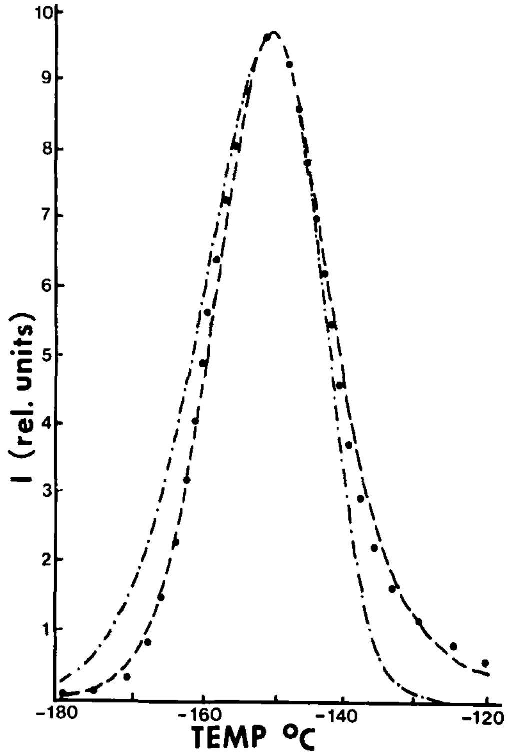

FIGURE 3 Low temperature peak from supercooled (4–6). (a) ●●●● Experimental data. (b) —·—·— Single trap, first order kinetics. (c) — — — Single trap, second order kinetics.

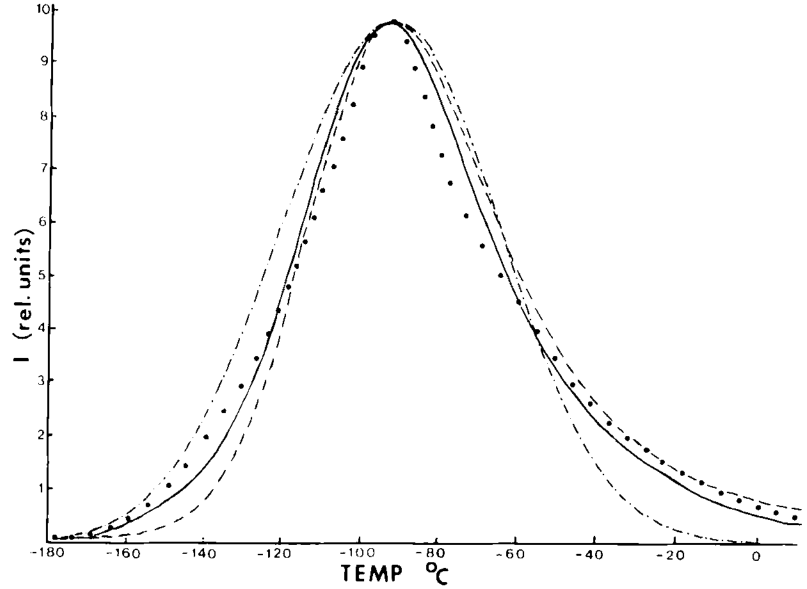

FIGURE 4 Low temperature RTL peak from crystallized (4–6) with overlapping peaks at −152°C and −27°C subtracted. (a) ●●●● Experimental data. (b) —·—·— Single trap, first order kinetics. (c) – – – Single trap, second order kinetics. (d) —— Lorentzian distribution of traps, second order kinetics.

single trap model using the technique of Mohan and Chen.[6] Figure 4 shows the comparable spectra and fit using data from the crystallized sample. It is apparent that neither fit is very good, the fit to the crystalline glow curve being particularly poor. There are several effects which can significantly distort a RTL glow curve, the most significant of these being: (1) The combining of electrons directly with ionized holes rather than via a constant number of available recombination centers, or the introduction of electron retrapping, either of which give rise to second order recombination kinetics.[6,7] (2) A distribution of trap energies about some mean trap depth E_0.

Also shown in Figures 3 and 4, and summarized in Table I, are the results of a least squares fit of the RTL data to models which incorporate respectively: (1) Second order recombination kinetics, (2) Assumed gaussian and lorentzian distributions of trap depths.

In utilizing a gaussian distribution of trapping energies, of the form $\exp(D(E_0 - E)^2)$, it rapidly became apparent that the spectrum obtained from said gaussian distribution about a mean energy E_0 differed little from the spectrum obtained from a single energy trap of lesser energy E_1. Since the spectrum obtained from a gaussian distribution of

TABLE I

	Supercooled 4–6	Crystallized 4–6
Single Trap		
First order kinetics	$E = .14$ ev $S = 1.00$	$E = .10$ ev $S = 1.00$
Second order kinetics	$E = .20$ ev $S = .06$	$E = .16$ ev $S = .33$
Gaussian Distribution		
First order kinetics	$E_0 = .68$ ev $D = 1218$ $S = .28$	$E_0 = .27$ ev $D = 451$ $S = .64$
Second order kinetics	$E_0 = .20$ ev $D = \infty$ $S = .06$	$E_0 = .16$ ev $D = \infty$ $S = .33$
Lorentzian Distribution		
First order kinetics	$E_0 = .64$ ev $B = 396$ $S = .39$	$E_0 = .25$ ev $B = 1387$ $S = .34$
Second order kinetics	$E_0 = .20$ ev $B = \infty$ $S = .06$	$E_0 = .24$ ev $B = 2800$ $S = .19$

energies about E_0 effectively mimics the spectrum of a single trap energy of energy E_1, and small variations in input data produce widely varying values for D and E_0, these parameters are not generally reliable when obtained from a fit of experimental data to an assumed distribution of this form. It is also apparent (Table I) that the assumed gaussian distribution does not provide the best fit to the experimental data.

An examination of several other distributions of trapping energies indicated that those with a greater portion of their total area in the "wings", such as the lorentzian distribution of the form $1/(1 + B(E_0 - E)^2)$, produced a spectrum which differed significantly from any spectrum obtained from a single energy trap and which produced an improved fit to the experimental data. The mean squared deviations of the theoretical curves from the experimental data are presented as "S" in Table I, normalized such that $S = 1$ for the first order single trap curve.

A final word is in order regarding the technique used to generate a RTL glow curve from a distribution of traps. The glow curve approximation given by Mohan and Chen for a single trap depth E involves the use of the temperature of the peak maximum T_m. When one introduces a distribution of trapping levels and numerically integrates over E, it is necessary to recognize that a change in the integration variable E will also involve a change in T_m. Hoogenstraaten[8] has shown that the relationship between an E and its associated T_m can be expressed as:

$$\ln T_m^2 - \ln E - E/kT_m = \ln T_{m0}^2 - \ln E_0 - E_0/kT_{m0} \qquad (1)$$

where the right side of the equation is a constant, T_{m0} being the temperature of the peak maximum associated with the mean trap depth E_0. Using this relationship, it is a straightforward procedure to integrate the single trap equation over any type of assumed trap distribution.

From Table I we note that the single trap, second order kinetics model provides a good fit to the observed glow curve from the supercooled sample. With the crystallized samples, however, it is apparent that a distribution of trapping energies is necessary to provide a reasonable fit to the observed glow peak. Again the second order kinetics, now associated with a lorentzian distribution of trap energies of full width at half maximum of .038 eV about a mean energy of .24 eV, provides the best fit to the experimental data.

RECOMBINATION ENERGIES

Whereas the above analysis allows the determination of the distribution of electron trapping energies, a measurement of the spectral distribution of the light emitted from the sample allows us to estimate the energy depth of the recombination centers below the conduction band.† Shown in Figure 5 is the measured spectral distribution obtained using an Oriel 7155 monochrometer, from both the narrow peak of the supercooled sample and that of the broad peak from the crystallized sample. In neither case is there any observed indication that either glow curve has a spectral distribution which changes with temperature. In both cases the recombination energy associated with the curve maximum is approximately 2.39 eV. It seems likely that the narrower spectal distribution of the crystallized sample is a reflection of the greater uniformity of molecular environments within the crystalline sample.

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† In the case, as seems possible from our analysis of the trapping kinetics, that the untrapped electron combines directly with the ionized molecule, then the ionized molecule is itself the recombination center and the associated energy is the energy difference between the conduction band and the highest filled molecular orbital of the unionized molecule.

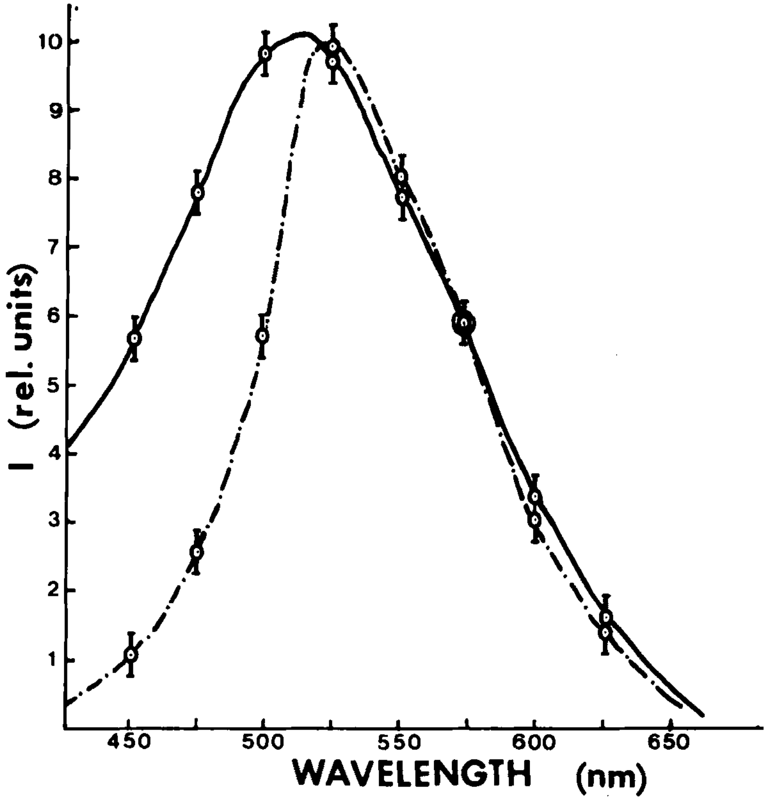

FIGURE 5 Spectral distribution of RTL glow curves. (a) —— Curve drawn through data from supercooled (4–6). (b) —·—·— Curve drawn through data from crystallized (4–6).

CONCLUSION

It has been possible to associate the single low temperature RTL peak from the supercooled sample with a second order glass transition at −152°C. Additional correlations are observed between the RTL spectra and the high temperature mesomorphic phase transitions.

The poor fit of the single trap first order kinetics model to the observed RTL peaks makes unlikely any trapping model based upon trapped electron-hole pairs (charge transfer excitons) or other thermally annealable long-lived excited states.[3] Also unlikely, as arising from similar first order kinetics, is the elementary model based upon untrapped electrons passing through the conduction band until falling into a constant number of empty recombination centers.

Two second order models, that of Garlick and Gibson,[9] in which there is an equal probability of the untrapped electron being retrapped as there is of it recombining with an empty luminescence center, and the model in which an untrapped electron travels through the conduction band until it combines directly with a hole, both give rise to second order curves which fit the observed data quite well. In the case of the crystallized sample it is necessary to introduce a distribution of trapping energies.

Acknowledgments

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