

Thermoluminescence in Solid Methane

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Thermoluminescence from both CH₄ and CD₄ doped with benzene or toluene (≤ 0.5 mol %) has been measured in the temperature region $10 < T/\text{K} < 40$. The methane was deposited from the vapour on a rotatable copper target, usually held at $T \approx 10$ K, and irradiated with ultraviolet light (predominantly of wavelength 2537 Å). Before the glow curves (emitted light intensity as a function of temperature) were recorded, phosphorescence and recombination luminescence from the specimens were allowed to decay isothermally. Certain sharp peaks in the thermoluminescence spectrum can be correlated with the known phase transitions in CH₄ and CD₄.

Under appropriate conditions, thermally-activated recombination of radiation-induced charged species in solids can give rise to luminescence. This thermoluminescence has been studied in both inorganic and organic solids and some correlation has been claimed to exist between peaks in the luminescence spectrum and solid-solid phase transitions.¹ More recently, the results of an investigation of radiothermoluminescence in eleven doped solid hydrocarbons, including methane, have been reported.² Some experimental factors such as sample size, glass-transition temperature and prior thermal treatment appeared to be important.

Experimental and theoretical study of solid isotopic methanes (CH_nD_{4-n}) has become rather extensive during the past few years.³ In part, this is because of a range of interesting phenomena that the solids exhibit: orientational ordering of the molecules; quantum crystal behaviour; conversion between nuclear spin symmetry species; negative thermal expansion and other lattice dynamical oddities. The current state of understanding of solid CH₄ is well-summarized in a recent article.⁴ Under its own vapour pressure, CH₄ forms two phases, the structures of which are, known:^{5,6} phase I, $T > 20.4$ K, space group *Fm3m*, 4 molecules per unit cell; phase II, $T < 20.4$ K, space group *Fm3c*, 32 molecules per unit cell. The deuterated methanes (and CH₄ under pressure) form a third solid phase, phase III, but its structure has not been fully established as yet. Theoretical calculations suggest⁷ the space group *P4₂/mbc* with 16 molecules per unit cell but this is not completely consistent with thermodynamic data obtained for phase III.⁸

The essential point is that, for the solid methanes, the changes in molecular arrangements that occur *via* the phase transitions are now reasonably well understood. In phase I, the molecules are orientationally disordered although there is some evidence⁹ that some orientational correlations persist in the temperature region a few degrees above the phase II → I transition point. In phase II, molecules on six of eight sub-lattices become orientationally ordered. Further ordering must occur in

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the formation of phase III but, as has been indicated, its exact nature is not yet completely established. Nevertheless, enough structural information is available overall so that it seemed appropriate to try to use it at this time to connect changes in thermoluminescence spectra with phase transitions in solid methane.

EXPERIMENTAL

CRYOSTAT

The cryostat, shown schematically in fig. 1 was a modified MD4A model made by Oxford Instruments. The flow of liquid helium from the main reservoir to a smaller pot beneath it could be controlled through a needle valve operated from the top of the cryostat. A copper plate of dimensions $20 \times 20 \times 2$ mm, on which the samples were vapour-deposited, was connected to the lower helium reservoir by a copper rod which provided good thermal contact.

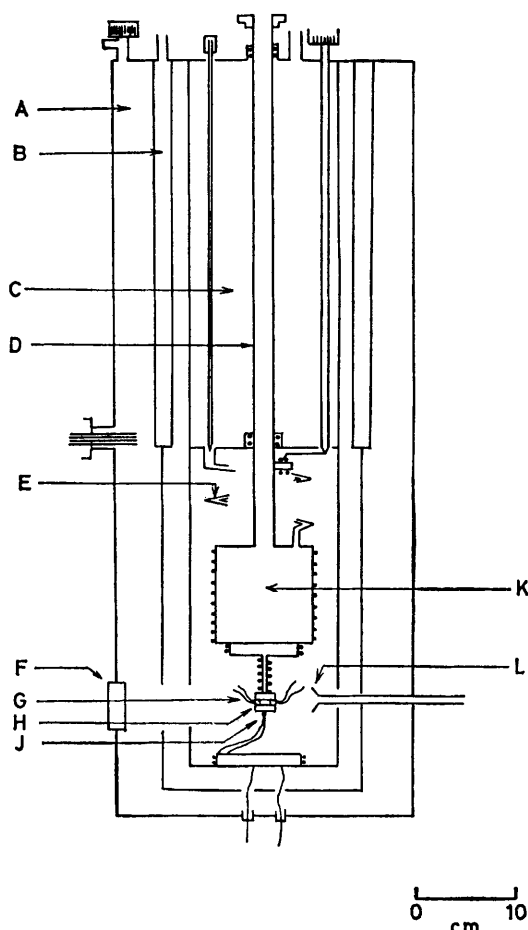


FIG. 1.—Schematic representation of the cryostat in cross-section. A, vacuum space; B, liquid nitrogen; C liquid helium; D, rotatable shaft; E, helium flow tube; F, optical window; G, Speer resistance thermometer; H, sample block; J, copper-constantan thermocouple; K, liquid helium; L, sample inlet tube.

The principal modification to the basic MD4A cryostat was the introduction of a rotatable shaft through the main helium reservoir. This insert carried the lower helium pot and the sample block, and was installed to allow the rotation of the sample block to face either the sample deposition port or the irradiation/light detection window without loss of vacuum or refrigerant. (O-ring seals at the top and bottom of the shaft made this possible.) The sample block was rotated with a screw mechanism at the top of the cryostat, and its position, as determined on a goniometer, was reproducible within 1° of arc.

A carbon resistance thermometer (Speer Carbon Co, St. Marys, Pennsylvania) was attached to the back side of the sample block, and was used to determine the sample temperature during the thermoluminescence measurements. The thermometer was first compared with a copper–constantan thermocouple that was attached to the bottom of the block. The thermocouple had previously been calibrated at 4.2 and 77 K, which was sufficient to fix the deviation of the e.m.f., characteristic of the particular constantan wire used, from a standard table. The thermocouple and the thermometer were intercompared over the region $13 < T/K < 38$, and gave absolute values of the temperature to within 0.5 K or better. At lower temperatures, copper–constantan thermocouples are rather insensitive and the resistance of the carbon thermometer was used in the well-known¹⁰ resistance–temperature relationship:

$$\ln R = A + B/T \quad (1)$$

where R is the resistance, T is the temperature in K and A and B are constants of the particular Speer thermometer. Eqn (1) was fitted to data for $13 \leq T/K \leq 20$, and gave the correct temperature down to 4.2 K to within 0.5 K, or better. The resistance–temperature relationship was reproducible over many cooling and heating cycles of the thermometer.

The lower reservoir was usually kept full of liquid helium during the sample deposition and irradiation procedures in order to maintain the sample block at its lowest temperature, which was 9.5 K because of the large heat input to the block. (The major source of this energy seemed to be radiation from the relatively warm sample inlet tube which was < 2 cm away from the sample block.)

To allow the temperature to rise during the thermoluminescence measurements, the needle valve to the lower helium pot was closed. When the liquid helium in the pot had evaporated, the temperature of the sample block rose in a smooth and reproducible fashion, as shown in fig. 2. A heater was wound around both the lower helium pot and the copper rod connecting the pot to the sample block and, after a thermoluminescence experiment, it was used to heat the block so that the sample could be pumped away. In addition, the heating rate for some experiments was changed by balancing the current through the heater and the flow of helium into the smaller pot.

SPECIMEN PREPARATION AND DEPOSITION

The CH_4 used was ultra-high purity grade (Matheson Gas, Whitby, Ontario), with a stated chemical purity of $\geq 99.97\%$. The principal impurities were N_2 and C_2H_6 ; no purification was performed.

The CD_4 (Merck, Sharp and Dohme, Montreal) was only $> 99\%$ chemically pure, and *ca.* 97% isotopically pure. It was not purified isotopically since the phase transition temperature in CD_4 does not critically depend on small amounts of CHD_3 . In some experiments, the cylinder containing the CD_4 was cooled to -78°C (dry ice + acetone) while a sample was removed. The experiments in which the CD_4 specimens were treated in this manner will be identified in the results section.

Reagent grade benzene and toluene, the doping agents, were dried over anhydrous CaCl_2 and fractionally distilled before being subjected to several freeze–pump–melt cycles on a high vacuum line to remove traces of dissolved gases.

The methane and the aromatic impurity, at pressures P_1 and P_2 , respectively, where $P_1 \gg P_2$, were allowed to mix for a few minutes in the gas phase, before the homogeneous sample was deposited onto the sample block. The spray-deposition of the sample took place through the tube that is shown in fig. 1. The wide-mouthed stainless steel tube was con-

nected *via* copper tubing to the sample reservoir on the outside of the cryostat and the flow of vapour into the cryostat was controlled by a needle valve. As the sample was deposited, the temperature of the sample block rose to ≈ 10 K or more, depending on the deposition rate (usually $2\text{--}20\text{ mg min}^{-1}$), due to the energy released on solidification. The specimens contained up to 0.5 mol % of aromatic impurity, and ranged in size from ≈ 5 to 300 μg .

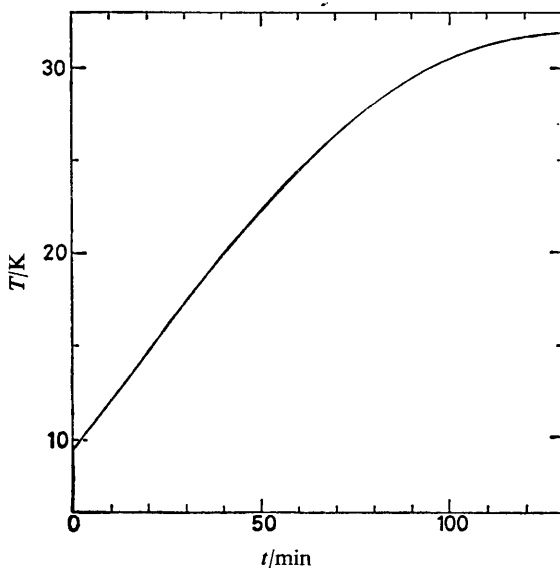


FIG. 2.—Typical heating curve for a thermoluminescence sample.

A freshly-deposited sample at its lowest temperature ($T \approx 9.5$ K) was a white translucent film but, as the temperature was increased during a thermoluminescence experiment, the sample took on a layered or flaky appearance.

IRRADIATION AND MEASUREMENT OF LIGHT EMISSION

A mercury pencil lamp (Spectronics Corp., Westbury, New York) of principal wavelength 2537 \AA , and with an intensity of $2 \times 10^{-3}\text{ W cm}^{-2}$ at a distance of 2.5 cm, was placed at the same optical window which was used for light detection, approximately 6 cm from the sample block. When the sample had been irradiated, the light was removed and the light detector immediately placed in position. (The delay between the end of the u.v.-irradiation and the detection of the emitted light was usually < 30 s.)

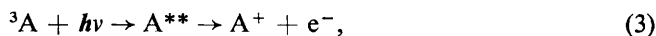
An RCA 6199 head-on photomultiplier tube was used to detect the light from the sample. The tube had its maximum sensitivity in the range $3000 \lesssim \lambda/\text{\AA} \lesssim 6000$, with an absolute maximum at $\lambda = 4400\text{ \AA}$. The tube output ($\approx 10^{-9}$ A) was amplified and recorded on a chart recorder.

To monitor the background response of the photomultiplier tube, a mechanical shutter mounted between the cryostat and the detector was closed and opened intermittently during the luminescence measurements.

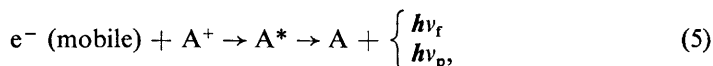
RESULTS

GENERAL ASPECTS OF THE LUMINESCENCE

It has been postulated¹¹ that the mechanism responsible for photothermoluminescence is as follows. Photoionization of a species, A, in the solid takes place such that A is excited by a two-photon process:



and an electron is produced. (Similarly, in radiothermoluminescence, X-rays, electrons or γ -rays bombard A to produce A^+ and electrons.) The electron that is produced can be trapped either at impurity centres (to form anions) or at lattice defects in the solid so as to lower the overall energy. This can take place either by changing the orientation of the neighbouring molecules (in the case of a polar medium), or by the induction of multipole moments in them (in the case of a non-polar medium).¹ The electron is trapped at a distance ≤ 100 Å from the parent cation¹ and, if additional energy is supplied, the two may recombine. In thermoluminescence, the electron may be detrapped by thermal energy,



and the result will be recombination of the mobile electron with the cation, A^+ , and fluorescence or phosphorescence that is characteristic of species A. Because of the high ionization energy of pure alkanes, a small amount of aromatic impurity must be added for photothermoluminescence to be detected in these matrices;¹ the aromatic compound then serves as species A in the above sequence. The presence of an aromatic impurity (benzene or toluene) was found to be essential to the observation of luminescence in the present experiments, and the so-called isothermoluminescence or ITL results support the above mechanism. The luminescence of benzene in various matrices at low temperatures has recently been characterized.¹²

Immediately following the deposition and irradiation of a methane + aromatic specimen, and before the temperature was allowed to increase, luminescence was observed. The light given off was of purple colour; a typical decay of the ITL is illustrated in fig. 3. Clearly, two processes are taking place, one short-lived and one long-lived.

Within ≈ 2 min after irradiation, the ITL decay is exponential with lifetimes consistent with those of solute phosphorescence ($\tau = 15$ s for benzene and 12 s for toluene, in either CH_4 or CD_4). As has been demonstrated,^{12,13} the phosphorescence lifetimes for benzene in CH_4 , N_2 and Ar are very similar. Although the spectrum of the emitted light was not determined in the present experiments, similar studies on other systems have shown it to be consistent with phosphorescence of the solute molecules.¹⁴

After the solute phosphorescence has decayed sufficiently, the ITL decay follows the relationship

$$I = kt^{-m}, \quad (6)$$

where k is a scaling parameter, and $m \approx 1$. A similar decay of the long-lived isothermal luminescence has been observed in many other solute + solvent systems, and is generally accepted to be due to the slow recombination of trapped electrons with cations.¹⁵⁻¹⁸ Whether the recombination takes place by diffusion or by electron tunnelling is a subject of much discussion; some other results aimed at elucidating the recombination mechanism will be discussed in detail elsewhere.¹⁹

THERMOLUMINESCENCE

Many factors, such as the sample size, heating rate and specimen preparation, have been reported to influence the glow curves of molecular solids, but they have not

always been studied systematically. The reproducibility of many of the earlier results can therefore be questioned. An attempt was made here to investigate these factors thoroughly; the present results will illustrate the limitations placed on the absolute determinations of a glow curve for a particular matrix + solute system.

Sugawara and Tabata² reported grossly different thermoluminescence curves for alkane + toluene samples when the size was varied from 5 to 30 mg. In the present experiments, the shapes of the glow curves for methane + aromatic mixtures were found to be independent of the sample size from 2 to 200 mg. (Representative glow curves for CH₄ + toluene are shown in fig. 4.) In other experiments that are not illustrated, heating rates were varied from those given in fig. 2 to a constant 0.14 K min⁻¹; the shapes of the glow curves remained unchanged although the positions

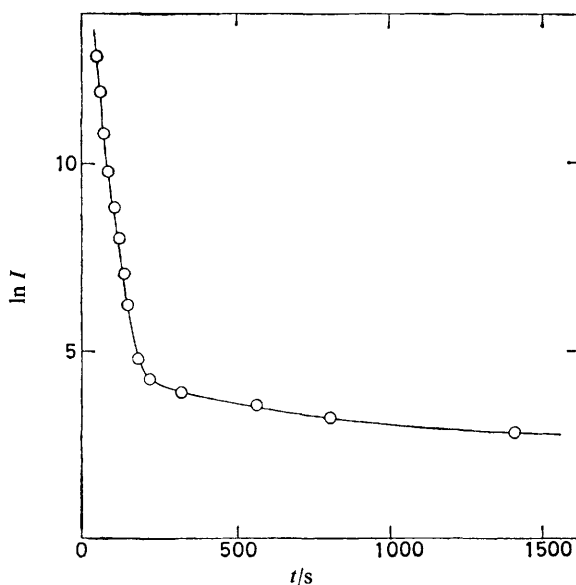


FIG. 3.—Decay of the isothermal luminescence. The results shown are for CH₄ + benzene at $T = 10$ K; the luminescence intensity is in arbitrary units.

of peaks shifted by as much as ± 1 K from one experiment to another. A possible source of the irreproducibility in the earlier work² may have been the extremely rapid heating rate used at low temperatures (as high as ≈ 20 K min⁻¹ at the start of the determination of a glow curve).

As illustrated in fig. 4, the shape of the glow curve of CH₄ + toluene was also independent of the solute concentration. This was true for all methane + aromatic samples used, over a solute concentration range 0.001-0.5 mol %. In fact, it can be seen from fig. 4 that the luminescence intensities are proportional to the total number of moles of solute present.

Although the vapour deposition method has been used to prepare glassy or non-crystalline samples of CH₃OH and H₂O,²⁰ it is improbable that glassy methane was formed here because extremely slow deposition rates were not used. (If the deposition is carried out rapidly, the heat released on solidification should provide sufficient energy to crystallize the sample.) In the present experiments, the deposition rate was varied by more than a factor of 10 without any change in the main features of the glow curves. This result indicated that the samples used were probably crystalline

and this was confirmed by the lack of dependence of the results on thermal treatment of the samples. (In solids which are known to form glasses, such as C_2H_5OH and $CH_3OH + H_2O$, thermoluminescence is strongly dependent on whether or not the samples were annealed.)^{21,22}

Variation of the solute, although not often considered in thermoluminescence studies, has been shown to have little effect on the shape of the glow curves of squalane²³ and polystyrene,²⁴ as well as of many other organic matrices.¹ The prevailing view appears to be that the presence of the solute only serves to increase the luminescence, but some specific effects were found in the present experiments. For example, we may contrast fig. 4 which shows the thermoluminescence glow curve for $CH_4 +$ toluene, with fig. 5, 6 and 7 which illustrate curves for $CH_4 +$ benzene, $CD_4 +$ toluene and $CD_4 +$ benzene, respectively. It is not surprising to see some dissimilarities between the glow curves for $CH_4 +$ aromatic and $CD_4 +$ aromatic because of the differences between the CH_4 and CD_4 phase diagrams, but the change of the thermoluminescence on substitution of benzene for toluene is remarkable.

The results for CH_4 indicate that more types of trapping sites are available in

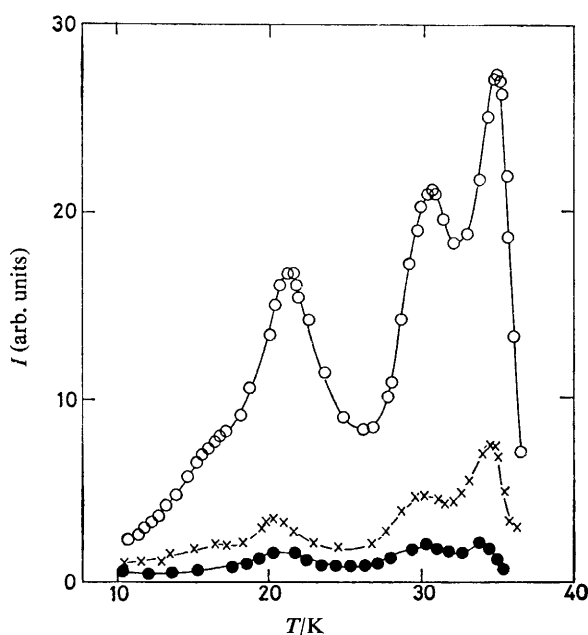


FIG. 4.—Effect of sample size and solute concentration on the glow curve. ○, 54 mg of $CH_4 + 0.008$ mol % toluene; ×, 12 mg of $CH_4 + 0.008$ mol % toluene; ●, 54 mg of $CH_4 + 0.0009$ mol % toluene.

$CH_4 +$ toluene than in $CH_4 +$ benzene. This can perhaps be reconciled with the possibility that the methyl group of toluene produces extra distortion of the matrix.

It can be seen from the results for CD_4 that extremely small amounts of extraneous impurities can also greatly influence the thermoluminescence profile. CD_4 untreated in any way and mixed with benzene always gave the glow curve displayed in fig. 7(a). On the other hand, when the cylinder containing the CD_4 was cooled in dry ice, the glow curve shown in fig. 7(b) was observed for 10 of 20 experiments; the other experiments yielded curves such as the one given in fig. 7(a). It is difficult to see that

the cooling procedure could have had any effect other than to promote preferential adsorption of an impurity (or impurities) on the cylinder wall.

DISCUSSION

The presence of both sharp and broad peaks in the glow curves indicates that two processes give rise to electron detrapping. Each of the broad peaks are attributable to one or more Randall-Wilkins processes,²⁵ *i.e.*, thermally activated recombination of electrons and cations. Our results illustrate that the distribution of the electron trap depths and the distance from the trapped electron to the parent cation depend

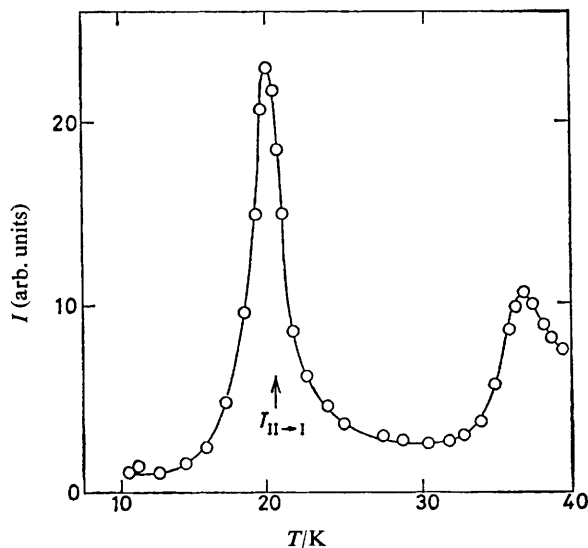


FIG. 5.—Glow curve of CH₄ + benzene.

on both the solute (benzene or toluene) and the matrix (CH₄ or CD₄) which were used. However, Randall-Wilkins peaks generally have widths which are $\approx 10\%$ of the peak temperatures (*i.e.*, $\Delta T/T_p \approx 0.1$),²⁵ and peaks which were much narrower than that were also observed. It is these sharp peaks which are of most interest here.

As noted in the introduction, CH₄ undergoes a transition from phase II \rightarrow I at $T = 20.4$ K. Similarly, CD₄ transforms from phase III \rightarrow II at $T = 22.0$ K and from phase II \rightarrow I at $T = 26.9$ K. From the results with benzene as additive, we see a clear correlation between thermoluminescence peaks and the solid-solid phase transitions: the sharp peak at $T = 20$ K in CH₄ + benzene and the shoulder and sharp peak at $T = 22$ K and $T = 27$ K, respectively, in CD₄ + benzene coincide with the transitions.

It is possible that the luminescence from accelerated recombination at the phase II \rightarrow I transition in CH₄ + toluene is masked by processes that are associated with the thermally activated electron-cation recombination, *i.e.*, with the Randall-Wilkins process. Sharp peaks from the phase-transition-induced recombination appear to be also absent in CD₄ + toluene. This system was not investigated in more detail because of the occurrence of Randall-Wilkins peaks in the regions where effects of the phase transitions would be expected to be seen.

Since it seems probable that the methane samples were crystalline, it must be

assumed that the phase transitions still take place in impure CD_4 ; perhaps the impurities bind tightly electrons that would otherwise be detrapped at the phase transitions.

At this time, we can only speculate about the microscopic processes that are responsible for the lowering of the barrier to electron-cation recombination at the phase transitions. Two obvious ones are changes in the arrangement of the centres of mass or in the orientational order of the molecules. Since the volume changes at the transitions are very small ($\approx 1\%$)²⁶ and since the basic crystal structure remains f.c.c. in the phase II \rightarrow I transition, it seems improbable that displacements of the centres

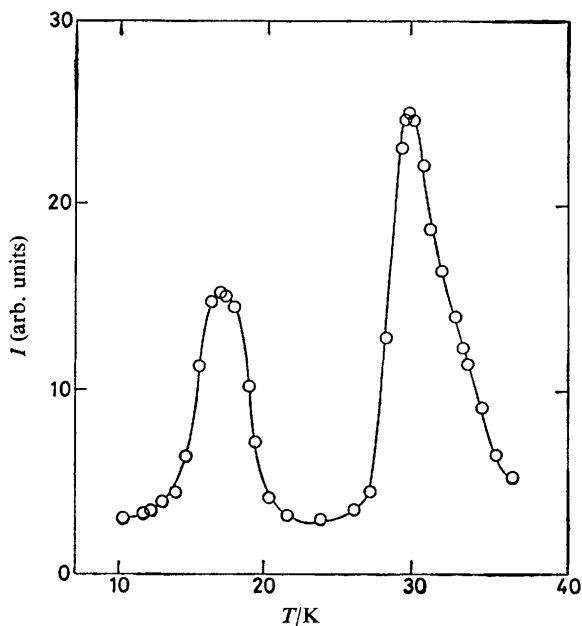


FIG. 6.—Glow curve of CD_4 + toluene.

of mass play a role. If orientational ordering/disordering of the molecules provides the basic release mechanism, it is then not surprising that extraneous impurity traps are so important. The energy changes corresponding to shifts of orientational order are very small ($< 100 \text{ J mol}^{-1}$).

In principle, the shapes and positions of the sharp peaks in the glow curves should provide information about the kinetics of the phase transitions. However, as noted earlier, the precise peak temperature varied by as much as 1 K from sample to sample. In addition, the peak width at half height ranged from 0.3 to 1 K for the phase II \rightarrow I transition in both CH_4 and CD_4 . These variations were probably caused by the existence of domain-type sub-structures in the samples with a resulting distribution of phase-transition temperatures. If the glow curve of a sample at a uniform temperature and in perfect thermal contact with the thermometer could be realized, a correlation between the peak widths and the two-phase coexistence region ought to be expected. (An X-ray diffraction study of CH_4 shows no appreciable temperature range of coexistence between phases I and II.²⁶ Similar experiments show a range of coexistence of 0.10 K for the phase III \rightarrow II and II \rightarrow I transitions in CD_4 .)⁶

CONCLUSIONS

This experimental study of thermoluminescence in solid CH_4 and CD_4 doped with benzene or toluene has established that the phenomenon is independent of factors such as sample size, solute concentration and prior thermal treatment. In these respects, the results differ from those of a prior study² of thermoluminescence in $\text{CH}_4 + \text{toluene}$. On the other hand, glow curves are found to be strongly dependent on the nature of the solute and on small amounts of extraneous impurities.

The technique of specimen preparation by vapour deposition was satisfactory for an exploratory type of investigation. The absence of a dependence of the shapes of

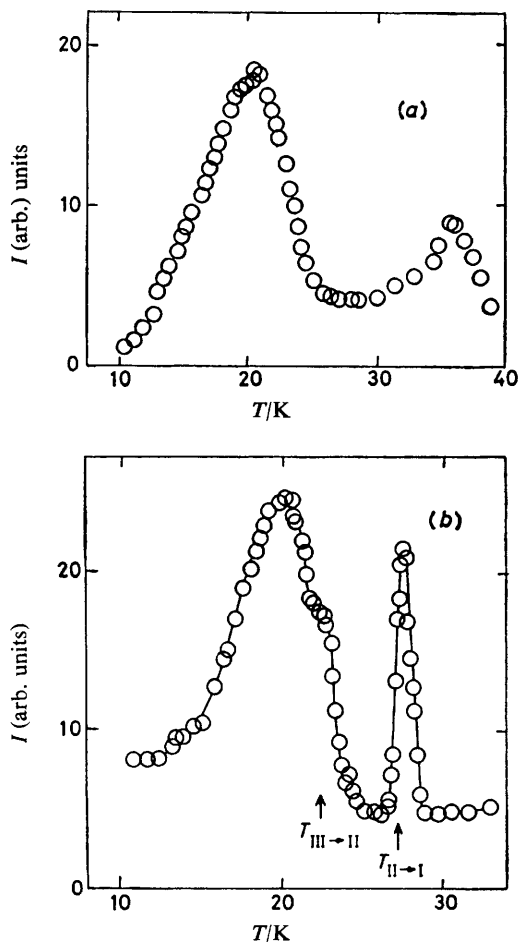


FIG. 7.—Glow curve of $\text{CD}_4 + \text{benzene}$: (a) untreated CD_4 ; (b) CD_4 cooled in dry ice.

glow curves on solute concentration indicates that the specimens had a uniform composition. To study peak shapes and positions more quantitatively, larger specimens whose temperatures could be controlled more accurately would be desirable. However, it would probably be very difficult to produce bulk specimens (even single crystals) of uniform solute distribution.

The results support the general proposition¹ that phase transitions can and do produce particular features such as sharp peaks in thermoluminescent spectra. But the recombination processes that lead to the abrupt light emission are strongly affected by traces of impurities. To extend the investigation, more attention would need to be paid to the purification of the materials.

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