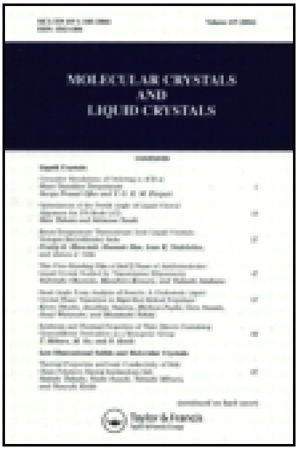

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Self-diffusion in Pure and Impurity Doped dl - Camphene

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To cite this article: N. T. Corke, N. C. Lockhart, R. S. Narang & J. N. Sherwood (1978): Self-diffusion in Pure and Impurity Doped dl - Camphene, Molecular Crystals and Liquid Crystals, 44:1-2, 45-60

To link to this article: http://dx.doi.org/10.1080/00268947808084967

Mol. Cryst. Liq. Cryst., 1978, Vol. 44, pp. 45–60

Printed in Holland

Self-diffusion in Pure and Impurity Doped dl-Camphene

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(*Received May 1, 1977*)

dl-Camphene has been ultra-purified and the process of self-diffusion in well-annealed crystals studied as a function of added dopants and temperature using radiotracer and plastic deformation techniques.

Impurities of equivalent size and shape to the host form solid solutions which do not perturb significantly the sub-structure of prepared crystals. As the size of the impurity departs from that of the host, segregation and precipitation occur either during or following solidification to yield an increased sub-grain-boundary and strain-induced dislocation sub-structure. In some cases this sub-structure was stable to annealing and the influence of a high equilibrium density of such imperfections on the self-diffusion process could be examined.

In the pure solid radiotracer self-diffusion proceeds in a manner similar to that observed for other pure rotator-phase solids. The introduction of imperfections produces the expected increase in overall diffusion rates and corresponding decrease in activation energy. These changes are mirrored by the plastic deformation experiments but not by a parallel pulsed n.m.r. examination. As found previously the latter yields results for both pure and imperfect samples which equate most closely with the radiotracer results for the defective samples.

Most studies of self-diffusion and plastic deformation in molecular solids have been carried out using highly pure, single crystalline material.[1] Little is known of the influence of impurities on these processes. In a previous publication Hawthorne and Sherwood[2] have noted an intriguing influence of impurity on the activation energy for plastic deformation of solid dl-camphene. The behaviour of the pure solid was similar, relatively, to that observed for other pure molecular solids. The introduction of impurities yielded a lower activation energy although the process was apparently still self-diffusion controlled. It was not possible to account for this change at the time.

dl-camphene is a member of the terpene series of organic compounds, many of which (including dl-camphene) form highly plastic, orientationally disordered phases (Plastic Crystals)[3] at temperatures near the melting point. Many members of the series have closely similar molecular structures. Consequently pairs of solids readily form solid solutions as evidenced by the phase diagrams. It seemed to us that a more detailed study of this solid using highly purified, single crystalline material and intentionally impurity doped material might shed more light on the previously observed variation and on the influence of impurities on the self-diffusion process in general. A further point of interest, is that it has been reported[4] that a broad-line n.m.r. examination of self-diffusion in pure and impure dl-camphene failed to parallel the previously observed variation in activation energy for plastic deformation. Values were obtained for pure and impure specimens which were equivalent to those obtained from the deformation study of the impure material. In view of the present general discrepancy between the results of radiotracer and n.m.r. studies of self-diffusion[1] it was thought that the extension of the examination to include a pulsed n.m.r. study of the same materials might indicate some reasons for this discrepancy both in general and in particular.

We report the detailed results of the structural, radiotracer and deformation experiments and briefly compare the results with those of the pulsed n.m.r. experiment, part of which has been reported[5] in detail elsewhere.

EXPERIMENTAL

Purification of materials

dl-Camphene Gas chromatographic analysis of commercial dl-camphene on a normal 2 m, $\frac{1}{4}''$ diam., column packed with 20% Apiezon L on 80/120 mesh siliconised celite revealed the presence of three major impurities (Figure 1). The removal of these by distillation and zone-refining yielded a sample which gave inconsistent results in later experiments. The presence of further impurity was suspected and a more careful analysis using a 50 m micro Golay capillary column with Apiezon L as substrate showed further impurities with retention times closer to the main peak than were previously resolvable (Figure 1). The removal of these was essential. A typical analysis is 0.7% cyclofenchene, 15–20% tricyclene, 1.5% α-fenchene, 0.3% cis p-menthane, 0.5% bornylene, 0.5% iso-camphene, 0.03% α-terpinene. In addition the sample was not optically pure.

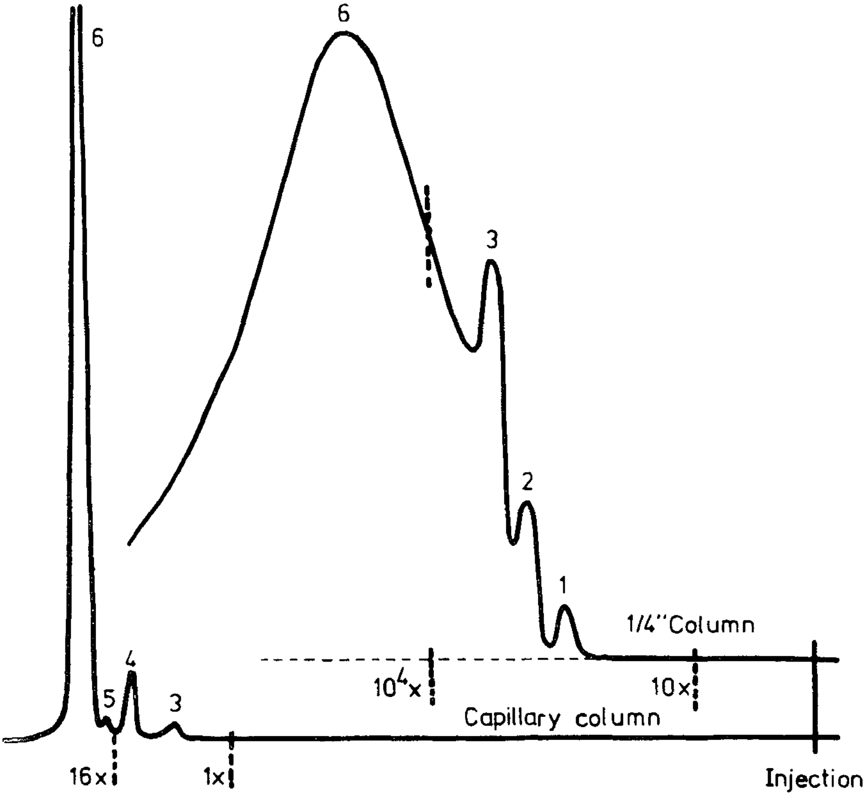

FIGURE 1 Typical chromatograms showing the increased resolution of the capillary column. 1. Cyclofenchene, 2. Bornylene, 3. Tricyclene, 4. Isocamphene, 5. α-Fenchene, 6. Camphene. The chromatogram shown for the capillary column was carried out using a sample partially purified by zone-refining and fractional distillation on a simple column.

Racemisation was achieved by refluxing the melt with 3.5% titanic acid. α-Fenchene (B.P. 432K) was converted to the β and γ isomers (B.P. 424K and 419K respectively) by boiling the racemised material with potassium bisulphate. The latter were more easily removed from camphene (B.P. 432.5K) by distillation. Zone-refining and normal fractional distillation were not efficient purification processes.

The crude material was distilled using a Nester Faust Spinning Band distillation column at a reflux ratio of 200:1. Several batches were collected the best of which contained no detectable impurity ($<0.001\%$).

The analysis of batches used in the current study were

A) 1.1% α-fenchene 0.3% iso-camphene
B) 0.8% α-fenchene 0.1% iso-camphene
C) <0.001%

Tricyclene Tricyclene was obtained by further distillation of the initial fractions using the Spinning Band column.

d-Camphor Commercial material was purified via the thiourea clathrate compound. A saturated solution of 1 mole camphor in 150 ml redistilled methanol was added to a refluxing solution of 3 moles of recrystallised thiourea in 2 l methanol. On cooling, a mass of fine white crystals was deposited. After filtration and washing with ether the camphor was liberated by boiling the crystals with water. Extraction with ether, removal of solvent, gradient sublimination and zone-refining yielded a material containing less than 1 ppm total impurity (g.l.c.).

Preparation of crystals

Crystals 1.5 cm diam. × 5 cm long were grown from the melt (camphene) and vapour phase (camphor).[6]

Dopants were added directly to the melt before growth and the crystals grown with stirring to promote an even distribution of impurity in the crystal. The final dopant distributions and hence segregation coefficients were determined by gas-liquid chromatography and freezing point determinations.

Radiotracers

Camphene-^{14}C (specific activity 1 μci mg^{-1}) was prepared by the method of Roberts and Jancey.[7]

Camphene-^{3}H was prepared by the racemisation of camphene[7] under the influence of an acid catalyst. 2 g of pyruvic acid was equilibrated with 1 ml (0.2 Ci) HTO and the excess water removed by distillation. 2.5 g of pure dl-camphene was added to the labelled pyruvic acid, the vessel sealed and heated at 150°C for 15 min. After cooling to room temperature the pale yellow material was diluted with 50 ml water and extracted with ether. The extract was washed with water and sodium bicarbonate solution and dried over magnesium sulphate. The ether was removed and the residue fractionally distilled. The product was purified by sublimation and zone refining to yield 0.5 g product (85% camphene, 15% tricyclene) of specific activity, 174 μci mg^{-1}. The presence of tricyclene is unavoidable. As shown below it is unlikely to interfere with the diffusion process. Both tracers yield identical behaviour.

Self-diffusion and plastic deformation studies

Serial sectioning experiments of radiotracer self-diffusion as a function of temperature and plastic deformation as a function of temperature were carried out as described previously.[8]

Microscopic examination

Microscopic examination of the etched and unetched surfaces of bulk crystals was carried out using interference contrast and phase contrast microscopy. Solvent etching with ethanol was used to reveal sub-grain boundaries, regions of segregated impurity and, possibly, dislocations (single etch pits). Due to the high plasticity of this solid and lack of cleavage it was not possible to prove an association between the single etch-pits and emergent dislocations. On initial etching however the pits were geometrically shaped (rhombic on $\{110\}$ faces), persisted on continued etching and formed characteristic alignments on strained crystal surfaces. Due to the very high volatility of the sample it was difficult to produce well defined photomicrographs (see Figure 3). On the basis of the above observations it does not seem unreasonable to associate the etch-pits with emergent dislocations.

RESULTS

Segregation experiments

The ease of incorporation of impurities into solid solution will depend on the chemical and physical similarity of the host and guest molecules. Thus in the present case d- and l-camphene (I and II Figure 2) form a continuous series of solid solutions and mixtures show similar behaviour to the pure isomers. Of the impurities present or added, tricyclene (III) forms a continuous series of solid solutions with the racemic camphene. Neither zone-refining or normal freezing yield any noticeable segregation, i.e., the segregation coefficient $k \simeq 1$. The close similarity of the molecules can be judged from the structural formulae.

The pure and tricyclene doped crystals have a low concentration of grain boundaries with average grain sizes circa 0.5 cm diameter. The dislocation content of carefully handled crystals, as evidenced by the solvent etch-pits is of the order of 10^4 to 10^6 cm^{-2} but can be increased to 10^8–10^{10} cm^{-2} on

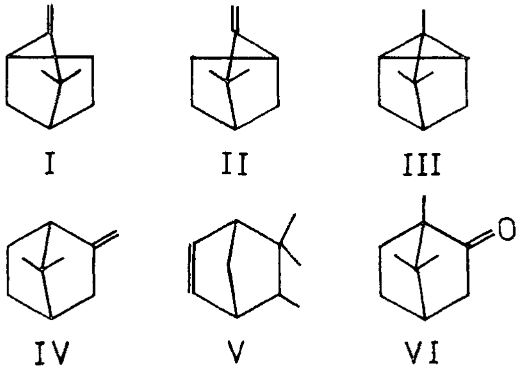

FIGURE 2 Structural formulae of the compounds used in the investigation. I. l-camphene, II. d-camphene, III. Tricyclene, IV. α-fenchene, V. Isocamphene, VI. d-camphor.

mishandling during or after growth. Attempts to assess the dislocation content of rapidly grown crystals proved impossible because the high etch-pit densities precluded satisfactory etch patterns. We estimate the numbers to be considerably in excess of $10^{10}\,\mathrm{cm}^{-2}$.

Neither α-fenchene (IV) ir iso-camphene (V) form solid solutions with dl-camphene. Both impurities yield a drastic lowering of the melting point of the pure solid. Normal freezing experiments confirmed that segregation did occur. From the impurity distribution we estimate that $k \simeq 0.8$ for both impurities. In the less pure solids (batch A and B) segregation of these impurities during crystal growth yielded a well-developed grain boundary structure average grain size 20–30 μm (Figure 3a). Etching revealed two types of etch distribution: single pits in increased numbers ($10^6 - 10^8\,\mathrm{cm}^{-2}$) and small regions of high pit density which presumably surround volumes of impurity precipitation in the solid (Figure 3b). Thus, segregation of impurities of this type generates an increased concentration of linear and planar defects in the solid. When these crystals or the pure crystals were subjected to small stresses a marked increase in the grain boundary content occurred (Figure 3c). There was also a strong indication of a considerable increase in dislocation content as evidenced by the appearance of slip traces on the crystal surface. Annealing near the melting point yielded grain growth but the crystal did not regain its original perfection. Rapidly frozen and annealed pure or impure material had a similar grain structure to that depicted in Figure 3c.

Although not an impurity in the original material d-camphor was also selected for doping experiments, since according to the phase diagram it forms a continuous series of solid solutions with dl-camphene. On crystal

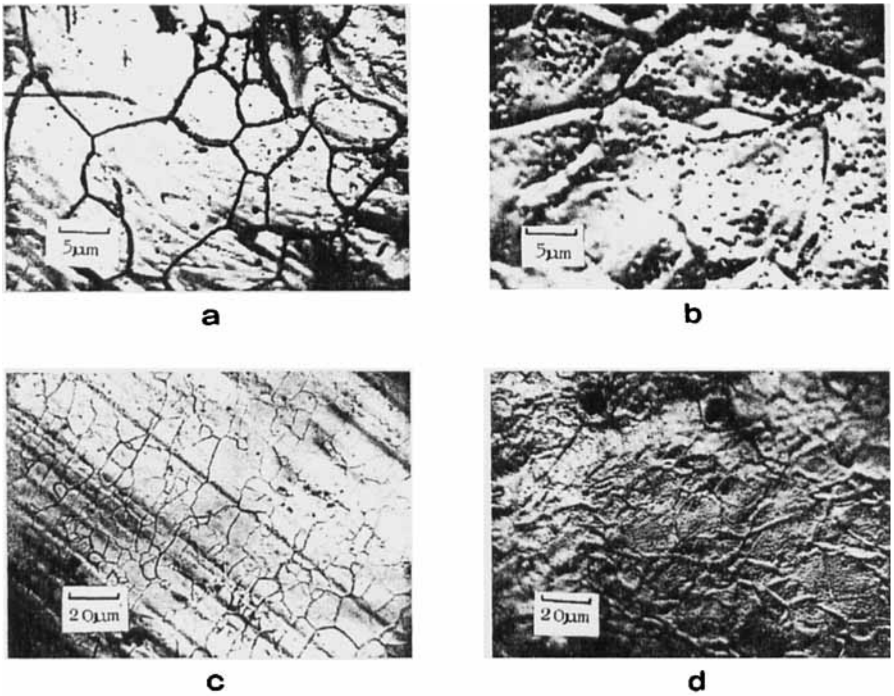

FIGURE 3 Photomicrographs of unetched and etched polished surfaces of crystals of pure and impure dl-camphene. a. Impure dl-camphene (batch A) showing the increased grain boundary structure (grain diam. ~25 μm) compared with that of the pure crystal (grain diam. ~5000 μm). b. Crystal as in a. etched in ice-cold methanol showing single etch-pits and pits grouped in areas of segregation (X). c. Deformed pure crystal (1% deformation) showing the resulting, greatly increased grain boundary structure and formation of slip traces and dislocation alignments. d. Crystal of pure dl-camphene doped with 5% d-camphor showing the stable grain structure and greatly increased number of etch-pits.

growth the d-camphor distributes through the crystals as depicted in Figure 4a. A large proportion (75%) of the added impurity concentrates in the first frozen half. The balance is fairly evenly distributed in the remainder. This distribution, and the evaluated segregation coefficient $k \simeq 1.7$ is consistent with the phase diagram. Much of this impurity segregates and precipitates from the crystal on cooling to yield an increase in grain and dislocation structure and in general disorder. Figure 3d shows the resulting grain size and general disorder in the upper portion of a crystal initially doped with 10% d-camphor, i.e., ~5% incorporation. Due to the greater compatibility of this molecule with the host, larger amounts of this impurity than α-fenchene and iso-camphene were required to generate parallel changes in defect

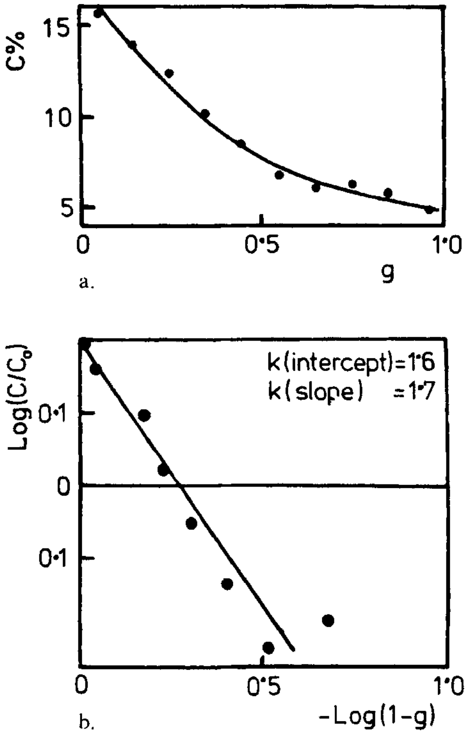

FIGURE 4 a. Distribution of d-camphor in a crystal of dl-camphene as a function of fraction crystallised (g). Initial concentration $C_0 = 10\%$, growth rate = 2 mm h^{-1}. b. Data of Figure 4a plotted according to the logarithmic form of the segregation equation log C/C_0 = log k + $(k - 1)$log$(1 - g)$.

structure. The grain size decreased with increasing d-camphor concentration. The resulting grain structure was stable to annealing.

Thus we conclude that good solid solutions are produced only where there is a close similarity between the host and guest molecules. Departure from this similarity results in an increasing tendency for the impurity to segregate from the solid either after freezing when the departure is small or on freezing when the departure is greater.

Plastic deformation

Plastic deformation offers the most rapid method of assessing the role of impurities and sub-structure in self-diffusion.[1] A survey was carried out in a series of pure and impurity-doped crystals. The latter were selected from those parts of the crystals where the impurity was most evenly distributed, i.e., the last frozen half. For secondary or steady state deformation the creep strain rate $\dot{\varepsilon}$ is related to the applied stress σ, activation energy E_c and temperature T by the expression

$$\dot{\varepsilon}T = A\sigma^n \exp(-E_c/RT)$$

where A and n are constants for all experiments. Values of the stress exponent n lay in the range 4–6 which is indicative of a self-diffusion controlled mechanism. Hence E_c should be equivalent to the activation energy for self-diffusion. The results of the survey are presented in Table I. In general, these results confirm those of the previous study[2] viz. addition of some impurities causes a change in the activation energy for the deformation processes from that characteristic of self-diffusion ($E_d \simeq 2L_s$ where the lattice energy $L_s = 51$ kJ mol^{-1}) to half that value in the highly doped material. There are several points of detail which influence the discussion.

1) Tricyclene has no effect on the process at concentrations up to 50%.

2) The residual impurities in batches A and B contribute to the lowering of E_c to a greater extent than camphor. Thus with 1.1% α-fenchene and 0.3%

TABLE I

Activation Energies (E_c/kJ mol^{-1}) and Stress Exponents (n) for Plastic Deformation in Pure and Impurity doped dl-Camphene

dl-Camphene/Tricyclene $n = 4$–5							
% Tricyclene	0	3	8	18	55		
E_c	94	98	98	104	92		
dl-Camphene/d-Camphor[a] $n = 4$–5							
Batch A: 1.1% α-Fenchene, 0.3% Isocamphene							
% d-Camphor	0	0.3	0.6	3.0			
E_c	87	77[b]	56	56			
Batch B: 0.8% α-Fenchene, 0.1% Isocamphene							
% d-Camphor	0	0.03	0.12	0.4	0.6		
E_c	98	93	79[b]	81[b]	45		
Batch C: 0% α-Fenchene, 0% Isocamphene							
% d-Camphor	0	0.6	1.2	2.5	3.5	5	5
E_c	96	99	75[b]	79[b]	76[b]	52	52
d-Camphor/dl-Camphene $n = 4$–5							
% dl-Camphene	0						
E_c	202	119	($L_s = 80$ kJ mol^{-1})				

[a] Percentages refer to the average concentration in the part of the crystal used for experiments.

[b] Average line from curved plots. For 0.4% d-Camphor in batch 2 the curvature varied from a slope of 84 kJ mol^{-1}, at high temperatures to 50kJ mol^{-1} at low temperatures.

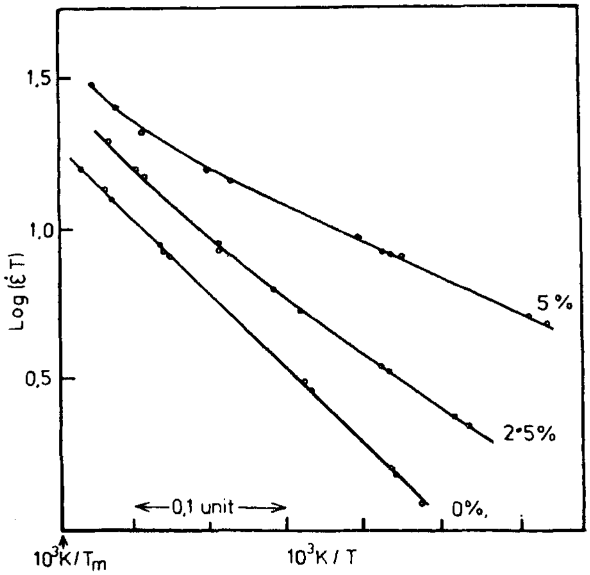

FIGURE 5 Normalised plots of log $\dot{\varepsilon}T$ against T^{-1} showing the influence of added d-camphor impurity on the activation energy for plastic deformation. At lower temperatures the intermediate line (2.5% d-camphor) converges on a line of slope equivalent to 45 kJ mol^{-1}, parallel to the values for the more highly impure samples.

isocamphene the change is provoked by an additional 0.5% d-camphor whilst the highly pure material requires the inclusion of 5%.

3) The change from one extreme of activation energy to the other is gradual and the plots of log $\dot{\varepsilon}T$ against $1/T$ which yield the intermediate values show some curvature to the extreme values at high and low temperatures. This is depicted in Figure 5.

4) A parallel impurity effect is noted at the other extreme of the dl-camphene/d-camphor system.

5. Whereas concentrations of tricyclene up to 50% yielded materials of similar plasticity to the pure solid other impurities caused a hardening of the solid, i.e., a greater stress ($\sim$10 times) was needed to produce an equivalent creep rate.

We conclude that whereas tricyclene forms apparently ideal solutions with the host, the remainder of the impurities introduce changes in the defect structure. These in turn lead to a change in the rate-controlling mechanism for deformation, i.e., in the observed diffusion rates. The generation of an excess concentration of point defects as suggested previously[2] is unlikely. This would lead to an increased plasticity which is not observed. A more reasonable proposal is that the change results from the gradual increase in dislocation and sub-grain boundary structure noted in the microscopic examination of the solids. Thus we propose, that in the pure solid, deformation occurs by lattice self-diffusion which dominates over the simultaneous processes of self-diffusion in grain boundaries and dislocations (pipe diffusion). The gradually increasing number of linear and planar defects in the impure solid leads to an increased contribution of pipe diffusion to the overall mass transport in the solid. Hence the transition to an activation energy more characteristic of the mixed process (or, in the extreme, pipe diffusion $E \simeq 1L_s$).[9] This overall self-diffusion process is still rate controlling in the deformation process, hence the stress exponent remains in the characteristic range. A similar argument has been used to account for changes in activation energy for creep in metals and ionic solids as the temperature is lowered.[10, 11] Presumably the diffusing vacancies encounter a sufficiently large number of "pipes" along their path from source to sink for the latter to effectively speed up the overall diffusion rate.

Self-diffusion

The above general behaviour was confirmed by radio-tracer experiments. Samples selected for examination were: pure dl-camphene, dl-camphene/15% tricyclene and dl-camphene/5% d-camphor. The last samples represent the extreme of extrinsic behaviour as indicated by the plastic deformation experiments. The dl-camphene used was the ultra-pure material. The method of evaluation of the data and performance of the radiotracer experiments have been adequately described previously.[8] Experiments with the pure material were carried out for periods sufficiently long to minimise grain boundary and dislocation contributions to the diffusion process. The resulting data are collected in Table 2 and Figure 6. ^{14}C and ^{3}H labelled tracers yielded similar results where both were used on the same material. Since the latter contains labelled tricyclene as impurity this confirms the compatibility of the camphene and tricyclene molecules in the lattice, a conclusion further emphasized by the excellent agreement between the pre-exponential factors and activation energies for the pure and tricyclene doped crystals. Similar experiments for equivalent periods using the d-camphor doped crystals yielded higher diffusion coefficients and a different temperature dependence. At temperatures approaching the melting point the diffusion coefficients became similar to those for the pure material. The relationship between the two sets of data (pure and d-camphor doped) is parallel to that noted for single and polycrystalline solids of other materials (e.g., silver[12]). To further confirm this possibility several short period experiments were carried out using more rapidly grown pure crystals. Under these conditions pipe diffusion

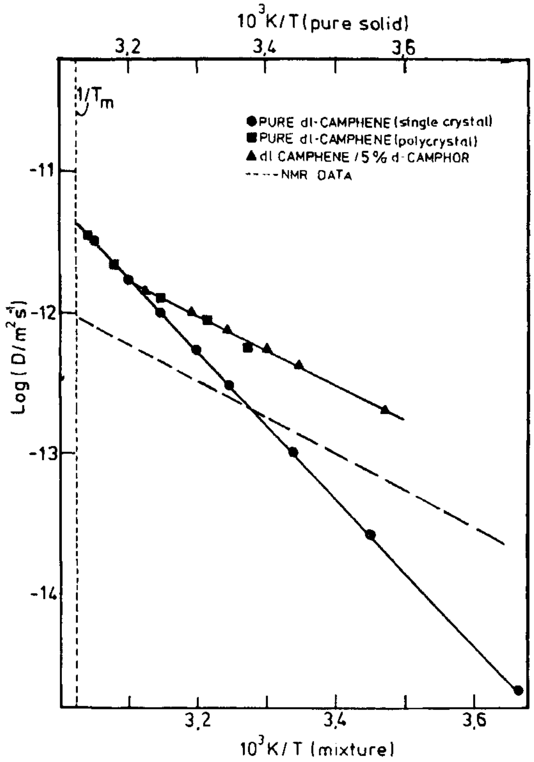

FIGURE 6 Log D against T^{-1} plots for the various samples used. The dotted line represents the position of the values calculated from the pulsed n.m.r. data as described in the text.

TABLE II

Pre-exponential Factors D_0(m^2 s^{-1}) and Activation Energies (E/kJ mol^{-1}) for Self-diffusion in Pure and Impurity-doped Camphene

Radiotracer	D_0	E
pure dl-camphene	2.3×10^4	97.8[a]
	2.0×10^4	96.2[b]
dl-camphene/15% tricyclene	1.2×10^4	89.0[a]
dl-camphene/15% d-camphor	2.5×10^{-4}	50.2[b]
Nuclear Magnetic Resonance		
pure dl-camphene	1.7×10^{-3}	56.5
dl-camphene/10% d-camphor	9.9×10^{-4}	56.2

[a] ^{14}C labelled tracer.
[b] ^{3}H labelled tracer.

will dominate. Self-diffusion coefficients evaluated from the initial portion of the diffusion profiles show a similar temperature dependence to that of the doped crystal. Attempts to evaluate pipe self-diffusion coefficients from the deeper penetration portion of the profiles were imprecise. The values of 10^{-8} to 10^{-9} $m^2\,s^{-1}$ obtained provide a measure of the magnitude of the interference from this process.

CONCLUSIONS

The self-diffusion parameters obtained from the radiotracer and plastic deformation studies on the pure solid are in excellent relative agreement with those derived from most previous studies of molecular solids.[1] From this parallel and the more particular similarity to the corresponding data in the b.c.c. organic solids hexamethylethane[8] and hexamethyldisilane[13,14] we conclude that lattice self-diffusion in dl-camphene occurs by a vacancy diffusion mechanism. This conclusion is confirmed by the recently published activation volume.[15]

In the impure solid there seems little doubt that the principal influence of added impurity is to generate an excessive concentration of line defects in the solid. These influence the overall molecular diffusion by providing short-circuiting paths along which the molecules can diffuse more rapidly and with lower energy than through the lattice. Thus we confirm and explain the results of the previous plastic deformation study of this material.[2] The difference between the present results and those of the broad-line n.m.r. examination[4] remains unresolved.

To provide a more precise comparison Boden and his co-workers[5] have carried out a pulsed n.m.r. examination on specimens of the pure and 10% doped material† used for the present tracer study. Full experimental details and the results for the pure solid have been published elsewhere.[5]

In general terms the results confirm those of the previous broad-line study. No distinction was observed between the behaviour of the pure and doped samples. Particularly significant was the observation that the data for both samples are best described by an isotropic diffusion model rather than the Torrey lattice diffusion model usually employed in the analysis of n.m.r. data.[5] This was also shown to be true for other low entropy of fusion solids, e.g., cyclohexane and hexamethyldisilane.

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† The doped sample will not be exactly equivalent to those used in the tracer study. In order to provide the necessary defect structure, the sample in the n.m.r. tube contained 10% d-camphor. The resulting "single" crystal would thus contain a distribution of camphor as depicted in Figure 4a. Successive melting and freezing would redistribute the d-camphor more uniformly but would yield a highly defective sample.

In the diffusion controlled region the evaulated correlation times for the pure and doped samples can be represented by

$$\text{pure } \tau = 4.6 \times 10^{-17} \exp(-56.5 \text{ kJ mol}^{-1}/RT) \text{ s}$$
$$\text{doped } \tau = 8 \times 10^{-17} \exp(-56.2 \text{ kJ mol}^{-1}/RT) \text{ s}$$

τ is related to the self-diffusion coefficient by the relationship

$$D = \overline{r^2}/8\tau$$

where $\overline{r^2}$ is the mean square diffusion jump distance. For vacancy diffusion on a b.c.c. lattice $\overline{r^2} = 3a_0^2/4$ where a_0 is the lattice parameter. The observation of an isotropic diffusion process suggests that for the n.m.r. $\overline{r^2} > 3a_0^2/4$, but it cannot be significantly greater in what is basically a crystalline lattice. Thus the use of the equivalence provides a set of minimum values of D (n.m.r.) for comparison with the present data. The mean line representing this variation is plotted on Figure 6 and the Arrhenius equation parameters quoted in Table II.

Within the experimental error and choice of $\overline{r^2}$ the values of D (n.m.r.) are approximately equivalent to those from all the tracer studies. However, their temperature dependence is quite distinct from that for the lattice diffusion coefficients and closely parallels the tracer data for the impure and polycrystalline solids. A similarity of absolute values for dynamic variables coupled with a difference in temperature dependence is not unknown when the correlation functions basic to the evaluation of the parameters are different.[16] Such an answer to the present discrepancy must be doubted however since excellent agreement is observed when similar analyses are used for the related materials, e.g., adamantane[17,18] and hexamethylethane.[8] On the other hand, it is impossible to ignore the marked parallel between the n.m.r. data and the tracer data for the impure and polycrystalline solid particularly in view of its occurance in other materials, e.g., defective cyclohexane,[19] phosphorus[20] and hexamethyldisilane.[13,14] The possibility of structural influences on the n.m.r. process must be considered.

Such an explanation is readily acceptable for the impure solid. The close similarity between these n.m.r. results, their behaviour and interpretation and those for the pure solid suggests a similar conclusion.

In the past convincing arguments have been advanced against this solution.[18] These have been based on the microscopically observable grain size and comparison with the structural properties of metallic solids. Concentrations of dislocations and other planar defects have been ignored. These are likely to be extremely high in the softer materials of low entropy of fusion where the discrepancy between tracer and n.m.r. diffusion coefficients is found.

The current evidence strongly indicates that the plasticity of these materials is adequately described by dislocation slip and climb.[21] Measurements of the bulk modulus of camphene[22] yield values of $\mu = 2.92 \times 10^8$ Nm^{-2} a factor of 10–100 times lower than metals and adamantane. From this we estimate[23] the line energy of the common dislocation slip system to be $E = \mu b^3 = 9.6 \times 10^{-20}$ J/molecule (0.6 ev/molecule) compared with 4.7 ev/molecule for adamantane. Thus it is not surprising that we find above that casual handling results in the introduction of considerable numbers of dislocations into these crystals. The number is highly likely to be in excess of 10^{12} cm^{-3} which Thomas[24] shows to be the limit at which the deformed dislocation cores in normal materials overlap and yield a crystal with all molecules displaced from the equilibrium position. The present crystals being much more plastic and possibly with wider dislocation cores could reach this limit at even lower dislocation concentrations. Even well below the overlap limit however a considerably greater proportion of the lattice could be "disordered" than is currently believed. As is shown in detail elsewhere[21] this property is shared by all materials for which there is a discrepancy between tracer and n.m.r. diffusion data.

We believe the situation to be as follows. In the well annealed crystal used for the tracer experiments at an equilibrium temperature the dislocation content will be moderately high. With careful experiment design true lattice diffusion can be observed. Rapid growth traps in a higher proportion of line defects which yield enhanced pipe diffusion at low temperatures. As the melting point is approached lattice diffusion dominates in experiments carried out for reasonably long periods and activation parameters more characteristic of this process result. Short period experiments in the same region however yield diffusion coefficients considerably influenced by pipe diffusion (see for example cyclohexane[19]). In the doped crystal the line defect substructure is stablized by the precipitation of impurity along the cores of the defects. Thus we see a mixture of diffusion in the cores and the disturbed matrix at all temperatures.

N.m.r. experiments are carried out on a relatively short time scale, thus even in the pure but still highly defective crystal it is possible that true lattice diffusion will not be observed; a conclusion reinforced by the necessity to invoke an isotropic diffusion model to explain the data. Furthermore experiments are normally made using quenched, polycrystalline samples subjected to thermal and mechanical strain due to temperature gradients and sudden temperature changes. This would be sufficient to generate continuously a high dislocation disorder in these highly plastic solids with the observed results. In the less plastic solids a less defective product results and better agreement is observed. Our current microscopic observations and more definite annealing studies of adamantane[25] show that even prolonged annealing is unlikely to restore the damaged crystal to an adequately perfect state. In any case n.m.r. experiments on pure single crystals show that even with the most careful handling the crystals may be too defective for the n.m.r. to reflect true lattice properties.[26]

We gratefully acknowledge the financial support of the Science Research Council through apparatus grants (JNS) and Studentships (NTC, NCL).

References

1. J. N. Sherwood, Specialist Periodical Reports C.S., Surface and Defect Properties of Solids, Vol. 2, p. 250, Chemical Society London, 1973.
2. H. M. Hawthorne and J. N. Sherwood, *Trans. Faraday Soc.*, **66**, 1799 (1970).
3. J. G. Aston, Physics and Chemistry of the Organic Solid State, Editors. D. Fox, M. M. Labes and A. Weissberger Interscience N.Y., 1963, Vol. 1, p. 543.
4. H. Blum and J. N. Sherwood, *Mol. Cryst. and Liquid Cryst.*, **10**, 381 (1970).
5. N. Boden, J. Cohen, and R. T. Squires, *Mol. Phys.*, **31**, 1813 (1976).
6. J. N. Sherwood, Cristallogenese Experimental Proc. Conf. French Assocn. for Crystal Growth, Rennes.
7. J. D. Roberts and J. A. Jancey, *J. Amer. Chem. Soc.* **73**, 3165 (1953).
8. N. C. Lockhart and J. N. Sherwood, *Faraday Symposia C.S.*, **6**, 57 (1972).
9. J. N. Sherwood and D. J. White, *Phil. Mag.*, **16**, 173 (1967).
10. P. G. McCormick and A. L. Ruoff, *J. Appl. Phys.*, **40**, 4812 (1969).
11. O. D. Sherby and P. M. Burke, *Prog. Mats. Sci.*, **13**, 327 (1967).
12. D. Turnbull, in Atom Movements, A.S.M. Cleveland, 1951, p. 129.
13. A. V. Chadwick, J. M. Chezeau, R. Folland, J. W. Forrest, and J. H. Strange, *J.C.S. Faraday I*, **71**, 1610 (1975).
14. P. Salthouse and J. N. Sherwood, *J.C.S. Faraday I*, in press.
15. P. McKay and J. N. Sherwood, *J.C.S. Faraday I*, **71**, 2331 (1976).
16. J. G. Powles, *Ber. Bunsengesselleschaft Phys. Chem.* **80**, 261 (1976).
17. E. M. Hampton and J. N. Sherwood. *Chem. Phys. Letters* **21**, 191 (1973).
18. H. A. Resing, *J. Chem. Phys.* **37**, 1575 (1962). *Mol. Cryst. Liquid Cryst.* **9**, 101 (1969).
19. E. M. Hampton and J. N. Sherwood, *J.C.S. Faraday I*, **72**, 2398 (1976).
20. P. McKay, E. M. Hampton, and J. N. Sherwood, *Phil. Mag.*, **30**, 853 (1974).
21. J. N. Sherwood, Specialist Periodical Reports, C.S. Surface and Defect Properties of Solid 6 Chemical Society, London 1977, in press.
22. J. R. Green and C. E. Scheie, *J. Phys. and Chem. Solids*, **28**, 383 (1967).
23. J. Friedel, Dislocations, Pergamon Press, London 1964, p. 74.
24. J. M. Thomas, *Advances in Catalysis* **19**, 202 (1969).
25. R. M. Hooper and J. N. Sherwood, to be published.
26. P. Bladon, N. C. Lockhart, and J. N. Sherwood. *Mol. Cryst. Liq. Cryst.* **19**, 315 (1973).