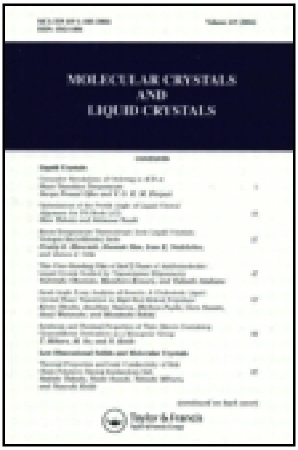

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Lattice Defects in Plastic Organic Solids
9. Nuclear Magnetic Resonance Studies of Translational Molecular Motion in Solids of Intermediate Entropies of Fusion

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Abstract—Studies have been made of the effects of temperature and sample purity on the c.w., NMR line narrowing behaviour at high temperatures for the following rotator phase organic solids of intermediate entropies of fusion: perfluorocyclohexane, triethylenediamine, 2-bromo-2, 3, 3′-trimethylbutane, 2-chloro-2,3,3′-trimethylbutane, 2,3-dibromo-2,3-dimethylbutane and tetra-(fluoromethyl)-methane.

The evaluated correlation times and activation energies for the solids of high entropy of fusion are equivalent to those for self-diffusion as measured by the radiotracer (or plastic deformation) technique. Proceeding to lower entropies of fusion there is a gradually increasing divergence between the two sets of data. It is proposed that this variation is a consequence of the way in which the different techniques reflect translational motion in systems with increasing defect disorder.

In a recent NMR line narrowing study of a series of rotator phase organic solids,(1) it was noted that there was a marked difference in the temperature dependence of the line-narrowing process between solids of high (~20 J mol^{-1}K^{-1}) and low (~8 J mol^{-1} K^{-1}) entropies of fusion. The former yielded correlation times and activation energies similar to those predicted for self-diffusion as measured by the radiotracer technique. The latter showed a completely different behaviour giving activation energies which were approximately one half of those predicted for self-diffusion. The reliability of the data at these extremes has been confirmed by later pulsed NMR measurements(2–5) and by further radiotracer measurements(6,7) on equivalent samples. In the previous study, two compounds with intermediate entropies of fusion, triethylenediamine and perfluorocyclohexane, showed a dual behaviour which could be deemed to be similar to that of the solids of high entropy of fusion at low temperatures, yielding to a behaviour more characteristic of the solids of low entropy of fusion at temperatures approaching the melting point. Both of these solids showed some characteristics in their line shapes and line narrowing behaviour which later studies(6) indicate could be associated with impurity effects. Thus, although impurity levels were below the limits of detection of other analytical techniques, the NMR signal was sensitive to the residual impurities. This could have yielded the noted curvature. In order to assess this probability we have purified perfluorocyclohexane, triethylenediamine and some other solids of similar entropies of fusion to levels at which the NMR signal no longer shows the influence of impurities and have repeated the measurements as a function of both purity and temperature.

1. Experimental

Materials

Commercially available 2,3-dibromo-2,3-dimethylbutane (DBME) was sublimed and gradient sublimed repeatedly to yield a sample containing ~360 p.p.m. total impurity.

2-bromo-, and 2-chloro- 2,3,3'-trimethylbutane (BME and CME) prepared as intermediates in the preparation of hexamethylethane,(7) were purified by successive gradient sublimations. (BME purity not known—decomposes on g.l.c. column, probably <50 p.p.m., CME <10 p.p.m.)

Perfluorocyclohexane (PFC) was subjected to repeated purifications as described previously(1) until a single NMR signal was obtained at all temperatures (<10 p.p.m.). Triethylenediamine (TED) was dried both by azeotropic distillation and by sublimation over calcium hydride and further purified as described previously.(1) Both methods of drying yielded a sample containing no detectable water. The former method also removes organic impurities not removed by the latter. The product, which showed similar behaviour to the previous sample,(1) was subjected to repeated gradient sublimations.

The final sample showed better characteristics and had no tendency to decompose on melting. Reproducible results were obtained on cycling through the melting point (<50 p.p.m.). Tetra(fluoromethyl)methane (TFFM) was prepared by the method of Gryskiewicz-Trochimowski.⁽⁸⁾ The product was gradient sublimed and zone refined (<10 p.p.m.).

The figures in brackets following each purification scheme indicate the minimum detectable total impurity content for each sample using gas liquid chromatography. The true purities will be better than these.

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NMR line narrowing,⁽¹⁾ radiotracer (BME)⁽⁷⁾ and plastic deformation (PFC, TFFM)⁽⁹⁾ studies were carried out as described previously over as wide a temperature range as was possible for the particular technique.

2. Results

The radiotracer result is a preliminary estimate—a more detailed report will be published later.

The plastic deformation rate ϵ' for PFC and TFFM showed the usual stress (σ) and temperature (T) dependence⁽⁹⁾

$$\epsilon' = A\sigma^n \exp - E_c/RT$$

where E_c is the activation energy. For both solids the stress exponents lie in the range 4–6 (PFC 5.2, TFFM 4.8) which indicates that vacancy diffusion dominates the process. Hence E_c is equivalent to the activation energy for self diffusion. The data quoted in Table 1 are the mean of several experiments.

The NMR signals for the pure solids were lorentzian in shape at high temperatures but became progressively more gaussian in shape as the line width approached the "rigid lattice" value at temperatures approaching the crystallographic transition. For pure PFC and TED the single signal persisted to the melting point. DBME and BME tended to decompose at temperatures close to the melting point. This was accompanied by the appearance of an " impurity spike " at the tip of the signal. CME and TFMM showed evidence

TABLE 1 Comparison of Correlation Times and Activation Energies for Self-diffusion in Organic Solids as Determined by Radiotracer/Plastic Deformation (*t*) and NMR (*n*) Techniques

	ΔS_M† J mol⁻¹ K⁻¹	ΔS_T† J mol⁻¹ K⁻¹	M_{2r} gauss²	τ_n° s	E_n kJ mol⁻¹	τ_t° s	E_t kJ mol⁻¹	L_s kJ mol⁻¹
Cyclohexane(1,7) (F)	7.9	36.0	1.1	1.2×10^{-15}	45.1 ± 2.1	1.1×10^{-22}	68.1 ± 1.3	41.8
Pivalic Acid(1,6) (F)	6.7	25.5	0.7	7.1×10^{-16}	55.6 ± 1.3	1.2×10^{-22}	91.2 ± 0.4	59
TFFM (F)	14.2	53.1	0.99	1.5×10^{-16}	64.8 ± 2.1	—	87.5 ± 4.0	43
PFC (F)	19.2	—	0.44	1.8×10^{-16}	60.7 ± 1.7	—	72.4 ± 5.3	37.6
TED (F)	17.1	30.1	1.2	4.8×10^{-18}	90.8 ± 2.5	—	—	56.3
BME (B)	21.7	22.6	0.77	4×10^{-18}	84.5 ± 2.1	1.6×10^{-20}	103.7	48
CME (B)	22.6	22.2	0.78	7×10^{-18}	80.3 ± 2.5	—	—	45
Hexamethylethane(7) (B)	20.1	13.0	0.91	2.4×10^{-20}	85.7 ± 2.1	3.3×10^{-20}	85.7 ± 4.1	43.5
DBME (B)	20	17.8	—	—	105.0 ± 5.0	—	—	53
Adamantane(12) (F)	20.9	16.3	—	1.6×10^{-21}	153.0	—	146.0 ± 0.4	63.2

B—b.c.c., F—f.c.c., † entropies of transition (T) and fusion (M) of the expected splitting of the signal at high temperatures due to spin–spin coupling but no impurity effects were noted in the signals for the pure solids. For all of the last four solids the results refer to those temperature ranges in which a pure lorentzian signal was observed.

All samples showed similar variations of line narrowing behaviour with increasing purity. This is well demonstrated by the results for TED and PFC in Fig. 1. The figure, which shows the full line width at half maximum height $\nu_{1/2}$ as a function of reciprocal temperature, refers to samples of reagent grade material (A), samples of equivalent

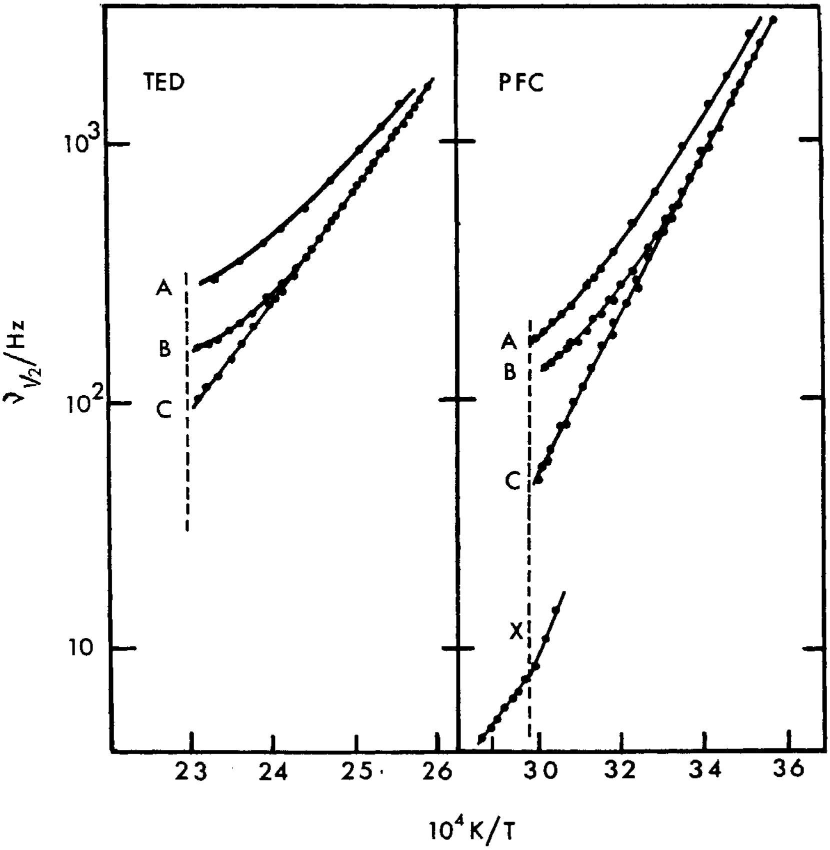

Figure 1. Plot of $\log \nu_{1/2}$ versus $1/T$ for PFC and TED. The separate lines show the behaviour of (A) reagent grade material, (B) purified material and (C) ultra pure material.

purity to those studied previously (B) and ultra purified samples (C).†

For PFC (A and B), in addition to the noted line broadening, a spike appeared at the tip of the line at high temperatures. Close to the melting point, the magnitude of the spike was sufficient to permit the accurate evaluation of $\nu_{1/2}$. The values (Fig. 1, X) are approximately equivalent to those expected for the liquid state. This suggests that the spike is associable with the motion of molecules in liquid like regions in the lattice, and could reflect grain-boundary pre-melting. The broadening of the main signal which occurs at temperatures below those at which the spike appears is more likely to be a bulk effect. It will be noted that where a curvature occurs, the low temperature portion is more characteristic of intrinsic behaviour. The experimental data for the remaining pure samples are presented in Fig. 2. DBME is not included since no fusion temperature can be

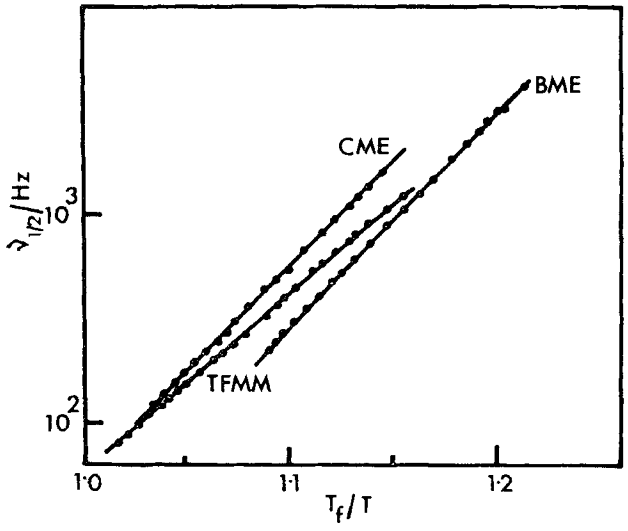

Figure 2. Typical plots of $\log \nu_{1/2}$ versus T_f/T, where T_f is the melting temperature, for BME, CME and TFMM.

† For TED and PFC (samples B and C) no absolute difference in purity could be determined. G.l.c. analysis showed no impurity in either sample above the minimum detectable limit—TED 50 p.p.m., PFC 10 p.p.m. The only distinction between the samples was the absence of an impurity spike on the NMR line at high temperatures for sample C.

measured for comparison. The $\log \nu_{1/2}$ versus $1/T$ plots for DBME were satisfactorily linear.

In the temperature range under study it is likely that the dominant intrinsic relaxation process is translational molecular motion. For a simple motional process $\nu_{1/2}$ is related to the spin–spin relaxation time T_2 by an expression

$$\nu_{1/2} = (\pi T_2)^{-1}.$$

This parameter can in turn be related to the correlation time τ_n for self-diffusion by the Torrey equation(10)

$$(T_2)^{-1} = AM_{2r}\tau_n$$

where A is a geometrical parameter and M_{2r} the effective intermolecular second moment for the rotator phase lattice. Using previously published (PFC,(3) TED(11)) or calculated (DBME, BME, CME, TFMM) values of M_{2r} (Table 1), we have evaluated the temperature dependence of τ_n

$$\tau_n = \tau_n^{\circ} \exp\left(-E_n/RT\right)$$

from the line narrowing data. The data are presented in Table 1 where they are compared with similar data calculated from the results of tracer and plastic deformation self-diffusion experiments and those of previous NMR studies(1,6,7,12) of compounds at the extremes of this range of solids. Where previous studies have been carried out on these solids the present data are in reasonable agreement with these. Thus for TED the present activation energy is in good agreement with a value published by Suga *et al.*(13) and is greater than a value published by Smith(10) for a sample which showed marked impurity effects. Figure 1 shows that impurities would have the effect of yielding a lower value for this parameter. Similarly, the data for PFC (C) is slightly different to that of Roeder and Douglass(3) for a less pure sample, but has been confirmed by a pulsed NMR measurement on the same sample.(14) Since, in addition to this, we find good agreement between our line narrowing data and those from pulsed studies on cyclohexane(1,3,6) pivalic acid(4,6) succinonitrile(15,16) and hexamethylethane,(2,5,7) we believe the present data to be reliably representative of the dominant molecular relaxation process in the solid within the error of the experiments.

3. Discussion

Figure 1 shows the considerable effects of small amounts of impurity on the line narrowing process for PFC and TED and confirms that the previously noted behaviour(1) was due in part to impurity effects. As indicated, this behaviour was common to all compounds studied and although confined to a c.w. examination there is no reason why pulsed NMR measurements should not be similarly affected. The gross result would probably be the evaluation of activation energies for the impure systems which are lower than the true values. Since the present impurity levels are below the limits of detection, it is impossible to be sure that truly intrinsic behaviour is being observed. The lack of impurity effects in the NMR signal, coupled with the trend of the line narrowing with increasing purity do support such a conclusion.

The complete results (Table 1) indicate that the present, pure, solids show a behaviour intermediate between those previously observed for the extremes, a gradual change being noted across the range of solids. This variation is also reflected in the values of the line width at the melting point which were 10 to 100 times higher for the solids of low entropy of fusion than those for solids of higher entropies of fusion.

Coupled with these variations in the NMR behaviour there is also a gradual divergence between the NMR and the tracer/creep data. The latter yield the generally noted equivalence, $E_t \approx 2L_s$(17) which is consistent with a vacancy type motion and provides a comparison where experimental data is not readily obtainable.

All of these changes parallel the gradual increase in general disorder in these solids from adamantane to cyclohexane as indicated by the variations in the relative entropies of fusion and transition. These entropies reflect all forms of structural and motional disordering. A more detailed association of this increase of disorder with self-diffusion has been shown by recent isotope effect measurements.(7,18) These experiments prove that the diffusing point defect in hexamethylethane is a lattice vacancy whereas in cyclohexane the defect involves many (12–20) molecules and can be described either as a small disordered region in the lattice or a vacancy into which the surrounding molecules have relaxed. Interpolation suggests a gradual variation in defect structure (increasing relaxation?) between these extremes. The relative differences between the values of τ_t° and E_t probably reflect this increased defect disordering and indicate that the overall tracer self-diffusion measurement is not too sensitive to this change. However, as the isotope effect measurement shows, much more complicated, highly correlated, translational motions occur with the disordered defect than for vacancy diffusion. We suggest that the current difference between the NMR and the tracer diffusion data is a consequence of this variation in defect structure; the proposed gradual increase of relaxation around the vacancies and the parallel increasing dominance of the associated molecular motions or interactions leading to the noted divergence.

Several experimental observations support this proposal. All the present solids yield similar line widths on melting (~1 Hz). Thus, in general terms, molecular motions and interactions must be similar for all the materials in the liquid state. In comparison, the line widths in the solid immediately prior to the melting point vary considerably from ~10 Hz for hexamethylethane to ~100 Hz for cyclohexane. Since the former exhibits vacancy diffusion and hence a simple hopping translational motion we can only assume that the broader line width in the solids of lower entropies of fusion results from an increasing complexity of molecular motions and interactions in the solid state. That this is associated with an increasing disorder can be inferred from the impurity effects noted above and previously. The impurities, which presumably induce lattice disorder by localized premelting or by lattice strain due to misfit lead to a much broader signal with a different temperature dependence than that for the pure solid. It does not seem unreasonable to speculate that a similar behaviour might result from intrinsic structural disorder in the pure crystal. In association with this we note that the relative temperature dependence of the broader, impurity induced, signal† is equivalent to that for the normal signal in the solids of very low entropy of fusion ($E_n \approx L_s$). We also recall that the addition of small amounts of impurity to solid camphene (low entropy of fusion) led to considerable changes in the plastic deformation characteristics of the solid.(19) There was no parallel change in the NMR line narrow-

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† The reference here is to the basic broadened signal and not to the " spike " which becomes perceptible at high temperatures.

ing(20); the width and temperature dependence of the signal being similar in the pure and impure solid. This observation, which has been confirmed by more recent radiotracer(21) and pulsed NMR studies,(14) strongly suggests that the NMR relaxation is dominated by some factor which is common to the pure and impure states. Although there is some experimental basis for our speculation, it is not possible at present to indicate how these variations in defect structure might affect the analysis of the NMR experiment. The initial impulse is to question the validity of the basic theory to describe the motion of the relaxed defect. The small variations in the radiotracer data suggest that the overall progress of the defect is not greatly dissimilar to normal vacancy motion. The usually accepted Torrey theory(10) is quite adequate to describe vacancy motion as is demonstrated by the excellent agreement between the radiotracer and NMR diffusion coefficients for hexamethylethane.(7) Some solids of lower entropy of fusion(2,4) also show the variations in relaxation behaviour predicted by the Torrey theory even though they do not yield agreement with the tracer data. This could be interpreted as indicating that the theory is insensitive to the proposed mechanistic changes. Alternatively, if this evidence is acceptable as proof that the theory holds, then it may be more appropriate to seek for the reason for the disagreement in the influence of concomitant molecular motions on the basic relaxation process or in the influence of changing molecular interactions in the disordered defect on the subsequent analysis.

More direct estimates of diffusion using spin relaxation can be derived from the pulsed field gradient technique which should be equivalent to the tracer method. Recent extensions of the technique have resulted in its use to estimate the self-diffusion coefficients of the solids cyclohexane and neopentane close to their melting points.(23) The results are in good agreement with those derived from pulsed relaxation time and c.w. measurements. If correct, this agreement would indicate that the NMR relaxation methods do reflect the basic translational motions of the spin labelled molecules and would suggest that these are different to molecular self-diffusion in these solids. Unfortunately, these measurements were made using very impure samples ($\sim 1\%$ impurity) in a temperature region where impurity contents as low as 10–100 p.p.m.(1,3) can yield premelting of disordering effects. Thus, at best, the values represent self-diffusion in an impurity disordered system and could equally well confirm that the relaxation methods reflect motion in the disordered state. Thus the result is inconclusive. That the experiment can be performed for such low diffusion rates is, however, notable and further studies on reliable systems as a function of temperature could aid in the solution of the present problem.

At present we can only conclude that the differences between the NMR and radiotracer studies of self-diffusion are a consequence of the different ways in which these methods reflect molecular motions in these partially disordered systems.

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