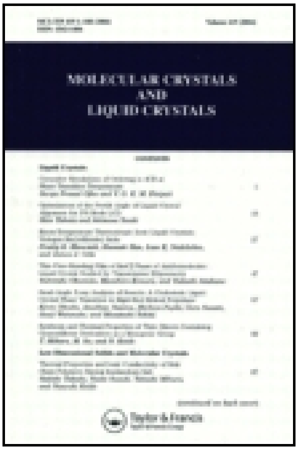

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On the Interpretation and Significance of Nuclear Spin Relaxation by Translational Diffusion in Organic Plastic Crystals

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On the Interpretation and Significance of Nuclear Spin Relaxation by Translational Diffusion in Organic Plastic Crystals

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Nuclear spin relaxation measurements in polycrystalline samples of the low entropy of fusion plastic crystals dl-camphene, cyclohexane and norbornylene are shown to be inconsistent with Torrey's random-walk model for lattice diffusion which has hitherto been used to relate these measurements to the mean time interval τ between consecutive molecular jumps; they are shown to be typical of an isotropic diffusion process. In contrast, measurements in polycrystalline perfluorocyclohexane, a high entropy of fusion solid, are consistent with the lattice-diffusion model. The implications of these results for the defect structure of plastic organic crystals is discussed.

1 INTRODUCTION

NMR methods have been used to study self-diffusion in a wide variety of organic plastic crystals.[1] These methods appear particularly suitable for investigating diffusion in these materials because of the pertinent magnitude of the self-diffusion coefficient D and polycrystalline samples can be employed. In all previous studies, Torrey's[2] random-walk model for uncorrelated isotropic diffusion in polycrystalline samples has been used to relate the measurements, T_1, $T_{1\rho}$ and T_2, to τ which is then related to D by $D = \langle r^2 \rangle / 6\tau$. The variation of D(or τ) with temperature is usually found to be according to $D = D_0 \exp(-E_D/RT)$. For solids with high entropies of fusion ΔS_f, e.g. hexamethylethane, there is apparent agreement between the values of D obtained in this way and those measured by the radiotracer method.[1] On the other hand, for low ΔS_f solids there are significant discrepancies between the values of D_0 and E_D as determined by the two techniques. While the radiotracer measurements appear to be self-consistent (in most cases $E_D \approx 2L_s$ and $f\Delta K \approx 0.7$ indicating a discrete monovacancy mechanism irrespective of ΔS_f), the NMR measurements reveal a gradual decrease of the ratio

E_D/L_s from 2 to 1 as ΔS_f decreases from 20 to 8 J K^{-1} mol^{-1} which has been attributed[3] to an inward relaxation of the molecules around the vacancies, but this should also be reflected in the tracer measurements. There is as yet no unequivocal explanation for the apparent discrepancies between the NMR and radiotracer measurements nor for the dependence of the NMR diffusion parameters on ΔS_f. We present in the following section NMR measurements which demonstrate that while Torrey's lattice-diffusion model is valid for the high ΔS_f solid perfluorocyclohexane (19.2 J K^{-1} mol^{-1}, fcc), it breaks down in the low ΔS_f solids dl-camphene (9.6 J K^{-1} mol^{-1}, bcc), cyclohexane (9.4 J K^{-1} mol^{-1}, fcc) and norbornylene (10.2 J K^{-1} mol^{-1}, hcp); the measurements in the latter materials are typical of an isotropic-diffusion process.

2 RESULTS

Figure 1 gives the proton T_1, $T_{1\rho}$ and T_2 measurements for polycrystalline dl-camphene. They are typical of those observed in other plastic crystals.[3] The spin relaxation due to translational diffusion was first analysed using Torrey's[2] random-walk model for lattice-diffusion, but, as seen in Figure 2, the fit is unsatisfactory. Wolf's[4] correlated monovacancy diffusion model does not fit the measurements either. A satisfactory fit could be obtained using the isotropic-diffusion model[2] with $\langle r^2 \rangle \gg d^2$ where d is the molecular diameter. Similar results have been obtained for cyclohexane and norbornylene as shown, respectively, in Figures 3 and 4, although in these materials, because of their relatively lower melting points, the uniqueness of a particular model is more difficult to establish. In contrast, the lattice diffusion model provides a consistent interpretation of the spin relaxation measurements in perfluorocyclohexane as shown in Figure 5.

3 DISCUSSION

We have shown that while the measurements in the high ΔS_f solid perfluorocyclohexane are consistent with Torrey's lattice-diffusion model, those for the low ΔS_f solids can only be satisfactorily interpreted in terms of an isotropic-diffusion process with $\langle r^2 \rangle \gg d^2$. A consequence of the latter condition is that the only mechanistic information obtainable from the spin relaxation measurements is that the molecules undergo random displacements with an undeterminable distribution of jump lengths about a mean which must be comparable to or greater than a molecular diameter.

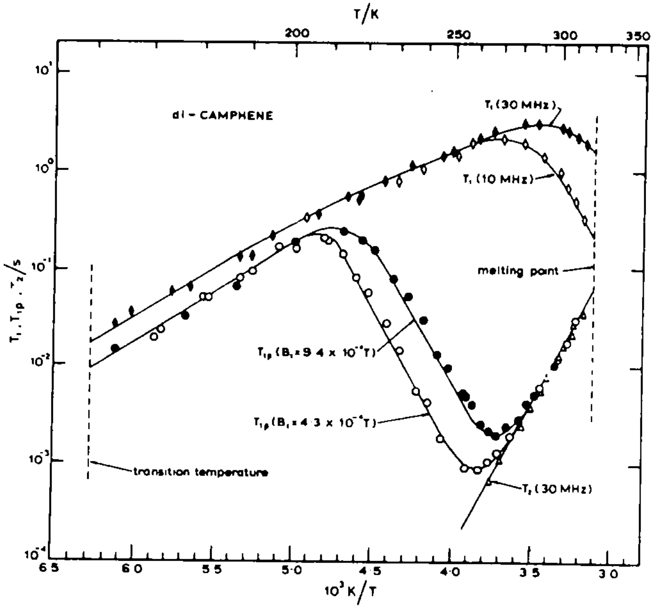

FIGURE 1

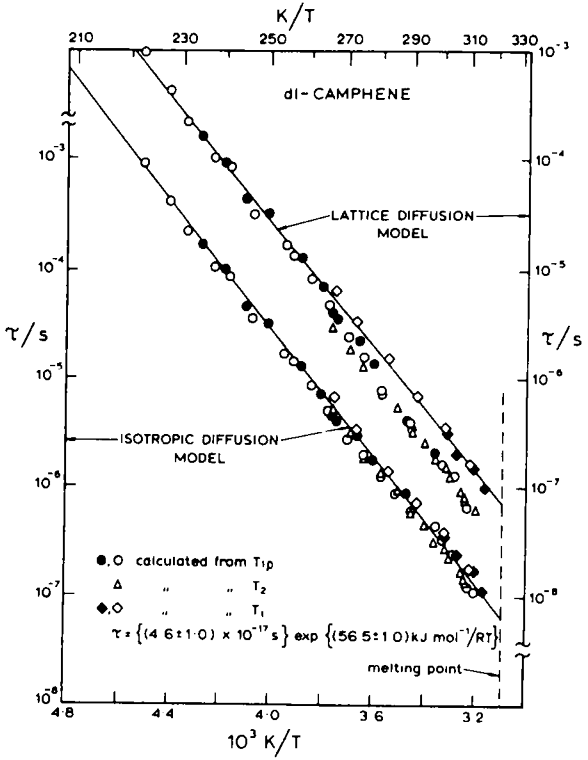

FIGURE 2

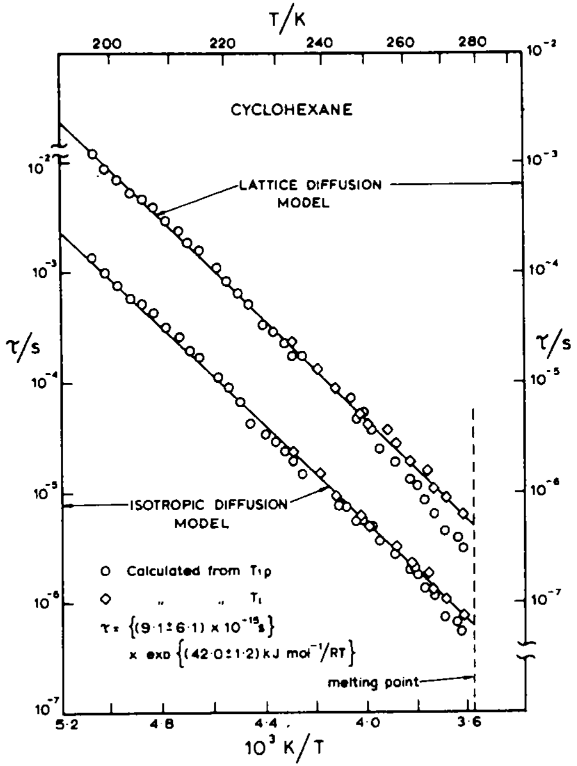

FIGURE 3

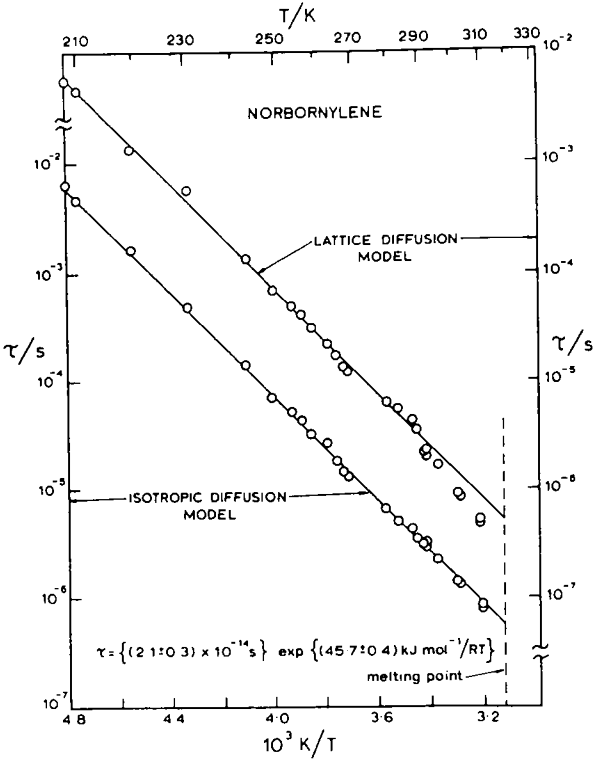

FIGURE 4

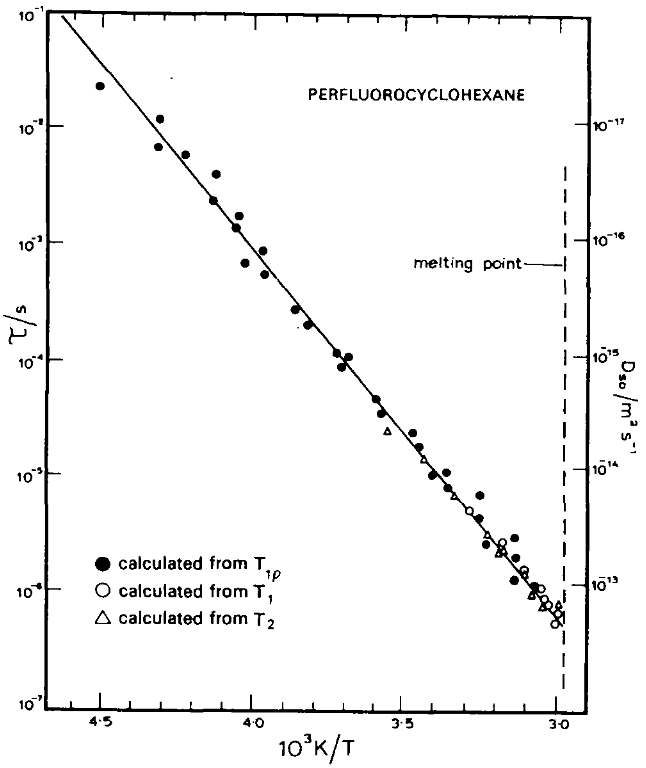

FIGURE 5

The values of τ for dl-camphene, given in Figure 2, are significantly different from those calculated from the radiotracer values of D[1]; $\tau_D = 3.8 \times 10^{-4}$ s exp(96.2 kJ mol^{-1}/RT)—note that $E_D \approx 2L_s$ ($L_s \equiv \Delta H_s = 51.0$ kJ mol^{-1}). Similar comparisons are not possible for cyclohexane and norbornylene. It is difficult to envisage how the NMR and tracer measurements can be reconciled in terms of any single diffusion mechanism. The only plausible explanation is that the defect structure of these polycrystalline low ΔS_f solids is fundamentally different from that of well annealled single crystals where the dominant defect is a simple lattice vacancy as shown by the radiotracer measurements.

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