

grade cyclohexane. In addition to the fact that  $T_{1\rho}$  allows measurement of much slower diffusion rates than is possible by measuring  $T_2$ , we note that the previous  $T_2$  measurement at atmospheric pressure and 257 K was 300 ms compared with later measurements on purified samples (Roeder and Douglass 1970) which gave  $T_{1\rho} \approx 1.0$  ms. ( $T_{1\rho}$  for low  $H_1$  and  $T_2$  should be equal at this temperature.) Our atmospheric pressure data agree with the more recent  $T_{1\rho}$  data.

Rice and Nachtrieb (1959) have proposed a law of corresponding states which, in the low pressure limit, has the form  $\ln D \propto T_f/T$  and which leads to the relation,

$$\frac{\Delta V^*}{\Delta H^*} = \frac{1}{T_f} \frac{dT_f}{dP} = \frac{\Delta V_f}{\Delta H_f}$$

The subscript f refers to the fusion parameters. This relationship holds well for metals and for the plastic crystal, white phosphorus (Nachtrieb and Handler 1955). In the case of cyclohexane the pressure dependence of the melting point is known (Babb 1963) enabling this relationship to be tested for an organic plastic crystal. Our measurements give  $\Delta V^*/\Delta H^* = 1.82 \text{ ml kJ}^{-1}$  which compares well with  $(1/T_f)(dT_f/dP) = 1.72 \text{ ml kJ}^{-1}$  at zero pressure. The value  $\Delta H^* = 41.4 \text{ kJ mol}^{-1}$  obtained by NMR is used in preference to the radiotracer value.

For pressures above 1.4 kbar  $\ln \tau$  does not vary linearly with pressure for cyclohexane and norbornylene. Further experiments are in progress to elucidate this apparent anomaly and will be discussed with a more detailed account of these experiments elsewhere.

The endospherical molecular reorientation, detected by its influence on  $T_1$ , is relatively insensitive to changes in pressure. The activation volumes which can be associated with this motion are  $5.3 \text{ ml mol}^{-1}$  for hexamethylethane,  $4.1 \text{ ml mol}^{-1}$  for norbornylene and  $3.2 \text{ ml mol}^{-1}$  for cyclohexane. These values are of the same order of magnitude as found in other molecular crystals (Anderson and Slichter 1966).

We tentatively conclude that in these three plastic molecular crystals, a single vacancy diffusion mechanism is dominant. Some inward relaxation of surrounding molecules is indicated in cyclohexane and norbornylene which have a low entropy of fusion and a close packed structure, but apparently not in hexamethylethane.

## References

- Anderson J E and Slichter W P 1966a *J. chem. Phys.* **44** 1797-802  
 — 1966b *J. chem. Phys.* **44** 3647-9  
 Babb S E 1963 *Rev. mod. Phys.* **35** 400-13  
 Baughman R H and Turnbull D 1971 *J. Phys. Chem. Solids* **32** 1375-94  
 Bladon P, Lockhart N C and Sherwood J N 1971 *Molec. Phys.* **20** 577-84  
 Breiting S M, Jones A D and Boyd R H 1971 *J. chem. Phys.* **54** 3959-64  
 Chadwick A V and Sherwood J N 1972 *Trans. Faraday Soc.* **68** 47-50  
 Chezeau J M, Dufourcq J and Strange J H 1971 *Molec. Phys.* **20** 577-84  
 Hassel O and Sommerfeldt A M 1938 *Z. Phys. Chem. B* **40** 391-5  
 Hood G M and Sherwood J N 1966a *J. Chim. Phys.* **63** 121-7  
 — 1966b *Molec. Crystals* **1** 97-112  
 Jackson R L and Strange J H 1972 *Acta. Crystallogr.* (to be published)  
 Jones G P 1966 *Phys. Rev.* **148** 332-5  
 Jost W 1960 *Diffusion* (New York: Academic Press) p 110

- Nachtrieb N H and Handler G S 1955 *J. chem. Phys.* **23** 1187-95  
Resing H A and Torrey H C 1963 *Phys. Rev.* **131** 1102-4  
Rice S A and Nachtrieb H N 1959 *J. chem. Phys.* **31** 139-45  
Roeder S B and Douglass D C 1970 *J. chem. Phys.* **52** 5525-30  
Scott D W *et al* 1952 *J. Am. Chem. Soc.* **74** 883-7  
Shewmon P G 1963 *Diffusion in Solids* (New York: McGraw-Hill) p 40  
Staveley L A K 1962 *Ann. Rev. Phys. Chem.* **13** 351-68  
West C D 1934 *Z. Kristallogr. Kristallgeom.* **88** 195  
Westrum E F 1969 *Molecular Dynamics and Structure of Solids* eds R S Carter and J J Bush (NBS Special Publication 301)