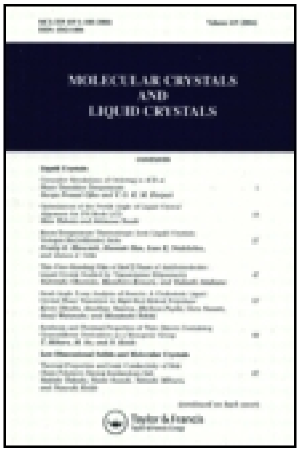

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: John R. Green & Donald R. Wheeler (1969): X-ray Investigation of Some Plastic Crystals II. Density of Vacancies in Cyclohexane, Cyclohexanol and dl-Camphene, Molecular Crystals, 6:1, 13-21

To link to this article: http://dx.doi.org/10.1080/15421406908082950

Molecular Crystals and Liquid Crystals. 1969. Vol. 6, pp. 13–21

Printed in Great Britain

X-ray Investigation of Some Plastic Crystals
II. Density of Vacancies in Cyclohexane, Cyclohexanol and dl-Camphene‡

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Received September 30, 1968; *in revised form January* 20, 1969

Abstract—X-ray powder photographs are used to calculate cell parameters for cyclohexane, cyclohexanol, and dl-camphene for a wide range of temperature. Comparison with the ordinary bulk density of cyclohexane and cyclohexanol leads to upper limits for the vacancy concentrations in these substances of 0.5% and 0.3%, respectively. Above about 10 °C the bulk density of camphene falls off markedly from what would be expected on the basis of the cell parameters. Comparison of the densities at higher temperatures with those to be expected either on the basis of the X-ray data or on the basis of linear extrapolation of the densities at lower temperatures leads to $\Delta H_v = 12.5 \pm 0.5$ kcal/mol and $\Delta S_v = 35 \pm 2$ e.u./mol for the process of vacancy formation. This value for the entropy implies that about 15 molecules gain additional freedom of motion every time one vacancy is formed. These results lead to predictions for the temperature variation in the ratio of molecular scattering factors for the 110 and 200 lines of camphene that are consistent with the observed ratios.

1. Introduction

Although many of the unusual properties of plastic solids can be understood by assuming a hindered rotation of the molecules about their equilibrium positions, there are some properties that

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‡ This work has been supported in part by the National Science Foundation.

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apparently can best be explained in terms of lattice defects. For example, Dunning[1] has suggested that the plasticity and high degree of molecular motion present in such organic crystals may be the result of an unusually large concentration of vacancies; also, Hood and Sherwood[2] have proposed a relatively high concentration of vacancies to account for the results of their investigation of the self-diffusion of cyclohexane.

It is, therefore, of interest to measure the vacancy concentrations in plastic crystals as directly as possible. Higgins *et al.*[3] compared the results of accurate measurements of density with the lattice parameters obtained from X-ray diffraction. It was mainly due to uncertainty in the X-ray data then available[4,5,6,7] that they were restricted to placing an upper limit of about 2 percent on the concentration of vacancies in several plastic solids including cyclohexane and cyclohexanol.

Our measurements of the lattice parameters allow us to place a lower limit on the concentration of vacancies in cyclohexane and cyclohexanol. Even more interesting, however, is the case of dl-camphene for which the concentration of vacancies becomes as large as a few percent.

2. Experimental

The experimental details of the X-ray diffraction measurements have been described in the preceding paper.[8] The cyclohexane obtained from Matheson, Colman and Bell had a melting point of 4.5 °C and was used without further preparation.

The macroscopic or bulk density of camphene was measured in a modified gas thermometer.[9] We also measured the density of cyclohexane and cyclohexanol in the same apparatus and compared the results with those reported by Higgins *et al.*[3] There are indications that our results may have a systematic error of a little less than one percent that varies with the accuracy of certain initial calibrations. This error affects the absolute accuracy of the results; but the relative accuracy of the different values obtained with a given run is still estimated to be of the order of a few tenths of a percent. Most samples were well annealed by having been cycled repeatedly between high and low temperatures; and in any case, differences in annealing histories had no observable effects on the densities within our expected errors.

3. Results and Discussion: Cyclohexane and Cyclohexanol

The lattice parameters measured for cyclohexane and cyclohexanol are listed in Table 1. These substances are known to form cubic structures in the plastic phase,[1] so there is no difficulty in indexing the powder diffraction lines and in calculating the lattice parameters.

TABLE 1 Lattice Parameters for Cyclohexane and Cyclohexanol

Cyclohexane:			
T(°C)	− 34.6	− 5.5	
a(Å)	8.677 ± 0.010	8.742 ± 0.007	
Cyclohexanol:			
T(°C)	− 27.0	− 5.7	+ 3.4
a(Å)	8.744 ± 0.001	8.770 ± 0.002	8.786 ± 0.006

If ρ_0 is the ideal density as calculated from the measured lattice constant on the assumption that every lattice site is occupied, and if ρ is the actual bulk density of the substance, then we can calculate the difference between the vacancy concentration c_v and the interstitial concentration c_i from the expression

$$c_v - c_i = (\rho_0 - \rho)/\rho_0. \quad (1)$$

In terms of the molal volume V, the lattice constant a, Avogadro's number N_a, and the number of lattice sites per unit cell n_1, this difference for a cubic structure is

$$c_v - c_i = 1 - N_a a^3/(n_1 V) \quad (2)$$

Higgins *et al.* give for the molal volume of cyclohexane the expression $V(C_6H_{12}) = 81.692 + 6.9343 \times 10^{-2}T$, where T is in °K and V is in cm^3/mol. Rather than use their quadratic fit for cyclohexanol, which indicates that there would be a minimum in the molal volume at 225 °K, we fitted their data to a linear expression: $V(C_6H_{11}OH) = 101.38 + 5.112 \times 10^{-2}(T - 260)$. The r.m.s. deviations of the quadratic and linear fits are both within the estimated experimental errors and are essentially the same. From our lattice parameters and from the bulk densities of Higgins *et al.*, we then calculate the difference $(c_v - c_i)$ as shown in Table 2. Since the close-packed structures of cyclohexane and cyclohexanol are not likely to contain any interstitials, the upper limits on their vacancy concentrations can be taken to be 0.5% and 0.3% respectively.

TABLE 2 Vacancy Concentration for Cyclohexane and Cyclohexanol

Cyclohexane			
T(°C)	− 34.6	− 5.5	
$c_v - c_i$	− 0.0018 ± 0.0065	+ 0.0038 ± 0.0045	
Cyclohexanol			
T(°C)	− 27.0	− 5.7	+ 3.4
$c_v - c_i$	− 0.0002 ± 0.0015	+ 0.0016 ± 0.0020	+ 0.0008 ± 0.0030

Previous direct determination of the vacancy concentrations for these two substances results only in putting upper limits at about 2%.[3] In a study of self-diffusion in cyclohexane, however, Hood and Sherwood[2] were able to deduce an estimate of 0.2 to 0.3% for the vacancy concentration in the temperature range of 246 to 276 °K through a chain of reasoning containing a number of approximations. Our more direct determination confirms their deductions.

4. Results and Discussion: dl-Camphene

The lattice parameters measured for dl-camphene in the rotational form are shown in Table 3. In an earlier paper[10] we commented on the unusual behavior of the ordinary bulk density of camphene. For temperatures above about 10 °C, the density begins to fall off appreciably from what one would expect from a

TABLE 3 Lattice Parameters for dl-Camphene

t(°C)	− 83.1	− 47.2	− 23.7
a(Å):	7.718 ± 0.001	7.806 ± 0.013	7.828 ± 0.005
t(°C):	− 5.5	+ 24.0	+ 27.5
a(Å):	7.868 ± 0.006	7.933 ± 0.008	7.941 ± 0.007

straight-line extrapolation of the densities measured at lower temperatures. We have confirmed this behavior in repeated measurements of the density in the modified gas thermometer apparatus. It now turns out that the densities that are calculated from the X-ray data do fall on the straight line extrapolated from the densities at lower temperatures. To demonstrate these behaviors quantitatively we present in Table 4 the results of fitting different groupings of the density data to different orders of polynomials in temperature. Densities are calculated from the X-ray data assuming that each of the two sites in the bcc lattice are always filled. It will be seen that the X-ray densities and the bulk densities obtained for temperatures below − 10° are in essential agreement. For both, going to a quadratic fit produces no significant improvement in the goodness of fit as measured by the r.m.s. deviations. The discrepancy of 0.7% between the constant terms for the two lies outside the error limits predicted from internal consistency, and is probably due to systematic errors connected with the use of the gas thermometer in measuring the bulk densities. In fitting the bulk densities obtained for the full

TABLE 4 Least Squares Fitting of Density Data (t °C)

1. X-ray data (6 points from − 83.1 to + 27.5 °C):
   $\rho = (0.9243 \pm 0.0015) - (0.695 \pm 0.034) \times 10^{-3} t$
   rms deviation: 0.0026
2. Bulk density (49 points from − 64.2 to − 13.2 °C):
   $\rho = (0.9311 \pm 0.0014) - (0.714 \pm 0.032) \times 10^{-3} t$
   rms deviation: 0.0040
3. Bulk density (87 points from − 64.2 to + 39.5 °C):
   $\rho = (0.9213 \pm 0.0015) - (1.360 \pm 0.054) \times 10^{-3} t - (8.9 \pm 1.2) \times 10^{-6} t^2$
   rms deviation: 0.010

range of temperatures from − 63.5° to + 38.8°, we find a significant improvement in the goodness of fit on going to a quadratic expression.

The falling off of the actual bulk density at higher temperatures from that predicted by the X-ray data and from that predicted by linear extrapolation of bulk densities at lower temperatures can be explained in terms of an increasing density of lattice vacancies at the higher temperatures. If the free energy for the formation of a lattice vacancy (per mol) is given by $\Delta G_v = \Delta H_v - T\Delta S_v$, where ΔH_v and ΔS_v are the enthalpy and entropy, respectively, of vacancy formation, we would expect the actual bulk density and the ideal X-ray density to be related by the expression

$$\rho = \rho_0[1 - \exp(-\Delta G_v/RT)] \tag{3}$$

Since we have both densities as functions of temperature, it is now possible to calculate values for the enthalpy, and entropy of vacancy formation. When we do this we obtain the values of 12.5 ± 0.5 kcal/mol for ΔH_v and 35 ± 2 e.u./mol for ΔS_v. We can estimate the heat of sublimation of camphene from vapor pressure data for the liquid and from the heat of fusion.[11] This turns out to be 11.2 kcal/mol, so that the energy of vacancy formation is then about 1.1 times the heat of sublimation.

The entropy of fusion is only 2.3 e.u./mol; consequently, there must be approximately 15 molecules involved every time a vacancy is formed. Since in the bcc structure there are eight nearest neighbors and six next-nearest neighbors, all of these must feel strongly the effects of the vacancy. With the above values for the enthalpy and entropy of vacancy formation, we calculate that at the melting point of 51 °C there should be a vacancy concentration of 7.7%. This with the participating number of 15 molecules per vacancy means that every molecule has relaxed into the liquid state.

We also find that the vacancy concentrations can be used to interpret the change with temperature of the molecular structure factors $[f_m^\circ(110)/f_m^\circ(200)]^2$ reported in the preceding paper.[8]

A plot of the experimentally determined ratios is given in Fig. 1. It will be recalled that these ratios have been corrected for the effects of thermal vibration, and would be constant if it were not for further thermal effects. We have just seen that for each vacancy formed about 15 neighboring molecules are strongly affected, If we assume that these 15 molecules change from the limited orientational freedom characterized by the 23 symmetry that was successful in predicting the observed ratios of molecular structure factors and that they gain the spherical symmetry that must characterize the relaxed state, we would expect the intensities from molecules in different states to be additive because of the random nature of the processes. In this case the ratio would be

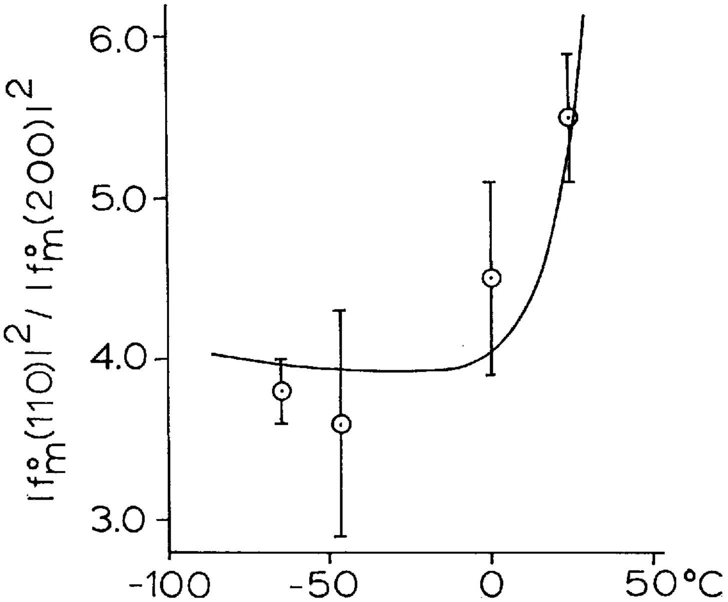

Figure 1. The ratio of molecular scattering factors corrected for thermal vibrations for the 110 and 200 lines of dl-camphene as a function of temperature. The curve is calculated on the basis of increased rotational freedom of the molecules resulting from vacancies at higher temperatures.

given by

$$\frac{[f_m^\circ(110)]^2}{[f_m^\circ(200)]^2} = \frac{15c_v[f_{m,ss}^\circ(110)]^2 + (1 - 15c_v)[f_{m,23}^\circ(110)]^2}{15c_v[f_{m,ss}^\circ(200)]^2 + (1 - 15c_v)[f_{m,23}^\circ(200)]^2}$$

Although the scattering factors vary slightly with temperature because of changes in the lattice constant, the main variation with temperature will enter through the vacancy concentration. The curve drawn in Fig. 1 is the result of substituting the appropriate molecular scattering factors into this relation together with the vacancy concentrations calculated on the basis of $c_v(T) = \exp[-(\Delta H_v - T\Delta S_v)/RT]$, with $\Delta H_v = 12.5$ kcal/mol and $\Delta S_v = 35$ e.u./mol. The agreement that results when we do this is such as to support our hypothesis of the unusually high concentration of vacancies in camphene. It might be expected that the relaxation of the neighboring molecules into the vacancies would have a large effect on the density; however, there are two indications that this effect need not be very large. First, there is the excellent linearity of the densities obtained from X-ray data over the entire range; second, we have seen in the preceding paper that in the case of cyclopentanol similar changes in orientational freedom can occur without large changes in crystal structure or density.

Except for the facts that camphene is 62% heavier than cyclohexane and that camphene has a double bond and a small dipole moment, the two molecules are rather similar. It is not surprising then that we should find a close agreement between our results for camphene and those obtained by Hood and Sherwood[3] in their study of self diffusion in cyclohexane. They obtained an experimental value for the enthalpy of vacancy formation in cyclohexane of about 11.4 kcal/mol; furthermore, they deduced that approximately 20 molecules are involved with each vacancy formed. Since the thermodynamic parameters are so similar, we might wonder why the behavior with respect to vacancy concentrations should appear to be so different. Actually, however, if we use the values for enthalpy and entropy of vacancy formation deduced for camphene, we find that *at the same temperature* the vacancy concentration for camphene is indistinguishable from that for cyclohexane. The apparently anomalous results for camphene thus appear to be due solely to the fact that camphene melts at a much higher temperature than cyclohexane

REFERENCES

1. Dunning, W. J., *J. Phys. Chem. Solids* **18**, 21 (1961).
2. Hood, G. M. and Sherwood, J. N., *Mol. Cryst.* **1**, 97 (1966).
3. Higgins, P. F., Ivor, R. A. B., Staveley, L. A. K. and Virden, J. J. des C., *J. Chem. Soc. London* 5762 (1964).
4. Post, B., *Acta Cryst.* **12**, 349 (1959).
5. Hassel, O. and Sommerfeldt, A. M., *Z. Phys. Chem.* **B40**, 391 (1938).
6. Schwartz, R. S., Post, B. and Fankuchen, I., *J. Amer. Chem. Soc.* **73**, 4490 (1951).
7. Cox, E. G. and Smith, J. A. S., *Nature* **173**, 75 (1954).
8. Green, J. R. and Wheeler, D. R., *this journal.*
9. Griffith, W. T., Dissertation, The University of New Mexico (1967).
10. Green, J. R. and Scheie, C. E., *J. Phys. Chem. Solids* **28**, 383 (1967).
11. Landolt-Bornstein, *Zahlenwerte and Funktionen* v. **2**, pt. **2a**, p. 97 (1960) and v. **2**, pt. **4**, p. 276 (1961) Springer, Berlin.