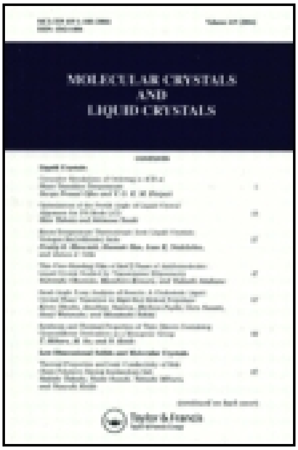

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Thermodynamics of Molecular Reorientationally Disordered Phases at High Pressure

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Thermodynamic properties of solid benzene and furan are investigated through Swenson's equation of state.

It is found that those two solids, in their dynamic disordered state, behave like cubic crystals from the thermodynamic point of view. In particular, this means that the crystal lattice configuration remains constant at constant volume, which is supported by previous high pressure low frequency Raman measurements.

This behaviour seems to be restricted to the reorientationally disordered phases.

The relations between thermodynamics, local crystal configuration and dynamic disorder in molecular crystals is discussed in terms of atom–atom pair wise potentials, Frenkel's model of molecular reorientations between discrete wells and the rotational diffusion model.

INTRODUCTION

Recently we have shown that a modified Bridgman's sylphon method can be used to directly measure P.V.T. data of orientationally disordered solids.[1,2] This method has been applied to solid orthorhombic benzene[1] in the range of pressure and temperature where orientational jumps of the molecules are known to occur between six indistinguishable orientations,[3,4] and to plastic pseudo-quadratic furan[2] where the disorder is dynamic and the allowed orientations distinguishable.[5]

The low frequency Raman spectra[6] and thermal expansivity[7] have also been investigated as a function of pressure and temperature for solid benzene in the same experimental range.

In this paper, we shall discuss the relations between microscopic (reorientational) properties and thermodynamic behaviour of both solid furan and benzene.

EQUATION OF STATE OF FURAN AND BENZENE

While investigating the P.V.T. properties of solid benzene[1] in the range 1 to 4000 bar and 250 to 350 K, we noticed that the isochoric P,T traces are linear and parallel, their slope, $(\partial P/\partial T)_V$, was of the order of 25 bar/K. We have also found that, for a given volume, all the isothermal traces have roughly the same slope; so, isothermal compressibility seems to be a function of volume only. These two results are supported by direct measurements of thermal expansivity, α, in solid benzene performed in the same experimental range.[7] In that work, it was shown that thermal expansivity is solely a function of volume in the whole range explored. In the same way, in solid furan,[2] PVT measurements revealed that the isotherms can be deduced from one another through a mere translation in the PV plane so that the isothermal compressibility was again a unique function of volume.

We should emphasize at this point that, in our opinion, PVT measurements alone do not provide a sufficient proof that the thermodynamic properties discussed here are valid, unless they are combined with other independent data, for instance direct thermal expansivity measurements (see reference 7). In this paper, we will mainly discuss the case of solid benzene for which sufficient data are available. The results obtained for plastic furan will only be considered as a clue that these properties could be valid for all orientationally disordered phases.

The three properties described above, which are not independent from one another, can be clearly understood through the equation of state proposed by Swenson,[8,9] following Frenkel's idea,[10] and applied to rare gas solids (RGS). This equation of state can be written as the sum of two terms:

$$P(V, T) = P_0(V) + P^*(V, T) \qquad (1)$$

where $P_0(V)$ is the static part of the pressure and $P^*(V, T)$ is the thermal part which vanishes at $T = 0$ K, as sketched in Figure 1.

Now, if the isothermal compressibility is a function of volume only, P^* is solely a function of temperature (see Figure 1). Then, equation 1 becomes:

$$P(V, T) = P_0(V) + P^*(T) \qquad (2)$$

This equation of state applies quite well to cubic simple solids (Swenson and coworkers),[8,11] and is also valid for both furan and benzene in their dynamic disordered state. Furthermore, if both isothermal compressibility and thermal expansivity are functions of volume only, then:

$$\left(\frac{\partial P}{\partial T}\right)_V = \text{constant} \qquad \text{(see appendix for demonstration)}$$

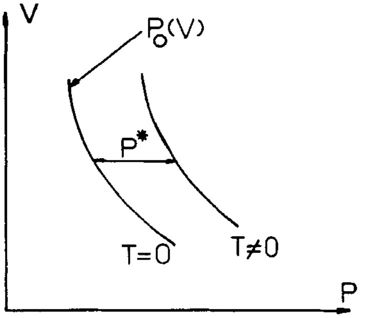

FIGURE 1 Schematic diagram explaining Swenson's equation of state in the pressure-volume plane. In this diagram P* is constant for a given temperature as it has been found for benzene and furan at high temperature, that is: P* is only temperature dependent.

This is the property which was observed in solid benzene *I*[1] as well as in RGS[12,13] at high temperature.

The reasons for this similarity between RGS and this orientationally disordered phase are discussed in the following section.

But we would like to examine quantitatively the applicability of Eq. (2) to solid benzene *I* in its whole range of existence. The first term in the right hand side of Eq. (2) is the absolute zero isothermal P, V path, which has been calculated theoretically (through a lattice dynamic method) by Ellenson and Nicol.[14] Unlike the isothermal paths we determined at high temperature, this absolute zero trace is not parallel to the high temperature isotherms. This is a first indication that isothermal compressibility can be considered as a unique function of volume only in the high temperature range, i.e. in the dynamic disordered state of solid benzene.†

The second term of Eq. (2), $P^*(T)$, can be calculated in a way analogous to Grüneisen's quasi-harmonic approximation, that is:[15]

$$P^*(T) = \gamma V^{-1} \int_0^T C_p \, \mathrm{d}T' \tag{3}$$

where γ is a mean Grüneisen-like constant defined through:

$$\gamma = n^{-1} \sum_i^n \gamma_i$$

where the γ_i's are the ordinary mode Grüneisen constants.

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† Experiments should be performed to determine at which temperature this property begins to hold.

Equation (3) has been used to calculate $P^*(T)$. The value of γ has been set at 2.5 after Ghelfenstein's Raman measurements.[16] Molar volumes at atmospheric pressure were taken from references 17 to 21 and constant pressure specific heat data, C_p, from Huffman's work.[22] The results of this calculation are shown in Figure 2.

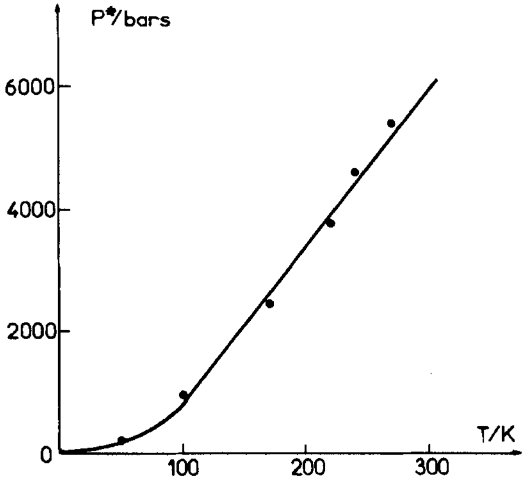

FIGURE 2 Calculated P* as a function of temperature. The curve is linear above roughly 100 K, its slope is 25.7 bar/K. The experimental value is 25 ± 2 bar/K.

The curve of Figure 2 can be viewed as the absolute zero P, T isochore, provided that external pressure P replaces internal pressure P^* (this is because $P_0(V)$ is equal to zero along this particular isochoric trace); so, we can see that, in our approximation, this isochore is linear at high temperature, its slope being 25.7 bar K^{-1}, which is almost the experimental value, (25 ± 2) bar K^{-1}.

Now, differentiating Eq. (2) we find:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P^*}{\partial T}\right)_V$$

Then, the isochores are all linear and parallel in the high temperature range (approximately above 100 K).

We can conclude that the quasi-harmonic approximation applies quite well to solid benzene at high temperature as it does to the RGS.[8,9]

We will now discuss the reasons why this property holds for both cubic RGS and solid benzene and furan.

MICROSCOPIC BEHAVIOUR

Recently, Ghelfenstein and Szwarc[6] have shown that, in the range 1 to 7000 bar and 238 to 328 K, a low-frequency Raman spectrum of solid benzene was not changed, as far as the mode frequencies are concerned, along a straight line they called "isospectrum" path. All the isospectrum paths are parallel in the range explored, their slope being 25 bar K^{-1}; so, the isospectrum paths are also isochoric traces for solid benzene in this range.

The fact that a low-frequency Raman spectrum remains unchanged at constant volume means that, as a first approximation, the distances between molecules and their relative orientations do not change. In other words, the lattice configuration remains unchanged at constant volume.

This result is unexpected for a molecular orthorhombic crystal like benzene. On the other hand, one expects this property to hold for a cubic atomic crystal, like the RGS, for which the configuration of the crystal lattice is not changed at constant volume indeed.

If we admit, as usual, that thermodynamic properties of molecular crystals can be described in terms of additive pair-wise atom–atom potentials, then it might be understood that, to any given lattice configuration, corresponds a unique isothermal compressibility value as well as a unique thermal expansivity coefficient, whatever the other thermodynamic parameters are. This explains why the same thermodynamic properties have been found for both RGS and solid benzene. In the case of plastic furan, a poor resolution of the Raman spectra did not allow us to draw any conclusions, but we expect the same properties to hold since the isothermal compressibility is solely a function of volume. As a matter of fact, we expect the properties to hold for all reorientationally disordered phases.

Furthermore, Ghelfenstein's Raman measurements on solid benzene show that, at low temperature, the isospectrum paths do not exist any longer. This provides a second indication that the thermodynamic features described in the first section are only valid in the dynamically disordered state of benzene. In the same way, no isospectrum path has been found in the Raman measurements in the rigid monoclinic γ-phase of *p*-dichlorobenzene.[24]

The question now arises whether the dynamic disorder is directly responsible for the existence of constant configuration isochores and, consequently, for the thermodynamic properties discussed above.

DYNAMIC DISORDER AND LOCAL CONFIGURATION

Whether orientational disorder can induce a constant configuration of the crystal lattice depends of course on the kind of the involved dynamic disorder. In the case of small globular molecules (for instance CH_4), for which the Pauling model of quasi-continuous molecular rotation holds, it can be understood that the mean relative orientations of the molecules remain constant at constant volume.

In the case of planar molecules like benzene and furan the rotation is no longer isotropic and Pauling model should be replaced by a "jumps between wells" model[23] (i.e. Frenkel's model). It is then more difficult to understand that the orientational jumps could lead to constant relative orientations of molecules. Moreover, this would not explain why the lattice parameters remain constant at constant volume in orthorhombic benzene. The same argument may be used when discussing the influence of dynamic disorder on thermodynamic potentials (heat content, free energy, . . .). According to Brot and Darmon,[23] the proportion of molecules in state of jump is always less than 1 % for solid benzene or furan, so energy functions should not be sensitive to the dynamics of this rearrangement.

The answer could be that both orientational disorder and "RGS-like" thermodynamics (local constant configuration) are two different outcomes of the same interaction properties in benzene and furan.

In any case, we are planning thermodynamic experiments in rigid cubic molecular crystals and in reorientational crystals of low symmetry to clear up this point.

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APPENDIX

Let us suppose that the isothermal compressibility, β, is a function of volume only. This means that the isothermal PV traces can be superimposed through a translation along the P-axis (see Figure 1). This condition can be written as:

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_P = 0 \tag{4}$$

This also means that all the isochoric PT traces have the same slope at constant pressure. If thermal expansivity, α, is a unique function of volume too, all the isochores are linear; that is

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta} \tag{5}$$

is a function of volume only.

Combining Eqs. (4) and (5) leads to:

$$\left(\frac{\partial P}{\partial T}\right)_V = \text{constant.}$$

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