Thermochimica Acta, 134 (1988) 35–39
Elsevier Science Publishers B.V., Amsterdam

DYNAMICAL ANALYSIS OF THE SPECIFIC HEAT IN P-DICHLOROBENZENE

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ABSTRACT

The temperature dependence of the specific heat in the α-phase of para-Dichlorobenzene is carefully analysed including anharmonic effects in the lattice modes. As a result, an excellent description of the data is produced, allowing the determination of the Debye temperature $T_D(cm^{-1})=106.2(1-13*10^{-4}T)$, and of a rotatory lattice mode $\nu_8(Ag)(cm^{-1})=42.9(1-5.2*10^{-4}T)$, both of them unknown. It is shown that both values turn out to be quite reasonable ones.

ANALYSIS OF DATA, RESULTS AND DISCUSSION

Paradichlorobenzene (PDCB, 1,4-$Cl_2C_6H_4$) is a polymorphic molecular crystal which exhibits three crystalline phases (1). Phase α is the one on which more data are available, and the one to be treated in this work. The α-phase is monoclinic ($P2_1/a$) with two molecules (Z=2) per primitive unit cell, therefore producing 72 normal modes of vibration which, at the Brillouin zone centre, may be divided in 60 internal and 12 external (2) modes. Since the internal modes exhibit small or negligible splittings and/or shiftings as compared to those of the free molecule, then the 60 internal modes will be taken as the 30 normal modes of vibration of the free molecule with a two fold degeneracy (in-phase and out-of-phase). These 30 frequencies are given in Ref. 3, and their values are (in cm^{-1}): 3095, 3086, 3070, 3065, 1574, 1570, 1477,

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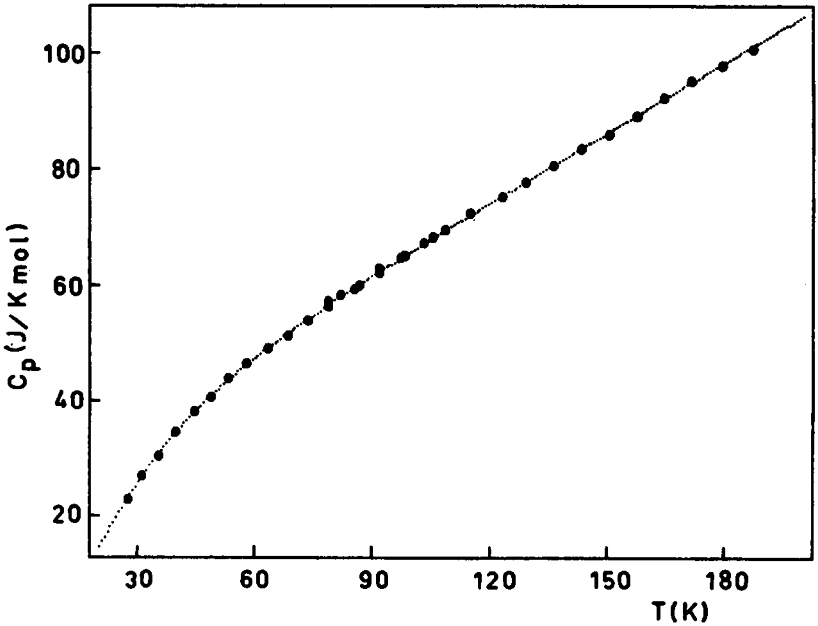

Fig.1: Filled circles depicted the C_p vs T data collected from Ref. 7, and corresponding to the frozen α-phase in the temperature interval where it is stable. The dotted line is that obtained by substituting into Eq. 1 the values indicated in the text as well as those deduced for the various parametres. As may be seen the agreement is excellent.

1394, 1290, 1265, 1169, 1107, 1092, 1084, 1015, 951, 934, 815, 747, 687, 650, 626, 550, 485, 407, 350, 326, 306, 226, 114. Dispersion across the Brillouin zone for these modes is neglected, and the same approximation is made for the 9 external optic modes (the remaining 3 external modes are acoustic). These 9 external optic modes may be divided in 3 translatory optic and 6 rotatory optic (3 in-phase and 3 out-of-phase). All but one of these modes have been reported at various temperatures (1,4,5), showing that they exhibit linear temperature dependences (4) which may be written (in cm^{-1}):

$\nu_1(Ag)=111.4(1-5.2*10^{-4}T)$ $\nu_1(Bg)=117.8(1-4.2*10^{-4}T)$
$\nu_2(Ag)=67.4(1-8.0*10^{-4}T)$ $\nu_2(Bg)=61.8(1-8.0*10^{-2}T)$
$\nu_3(Bg)=33.7(1-6.6*10^{-4}T)$ $\nu_4(Au)=27.4(1-1.7*10^{-4}T)$
$\nu_5(Au)=66.8(1-5.4*10^{-4}T)$ $\nu_6(Bu)=46.0(1-5.7*10^{-4}T)$.

The missing frequency is $\nu_3(Ag)$ which roughly correspond to out-of-phase rotations of the two molecules in a primitive cell about an axis contained in the benzene ring plane and perpendicular to the Cl(1)-Cl(4) (of the same molecule) direction.

The temperature dependence of the specific heat (C_p vs T) in PDCB is reported in Ref. 7, and the data selected out of this paper is depicted in Fig 1. These data correspond to that obtained for the frozen α-phase in the temperature interval where it remains stable. It is the aim of this paper, through a careful analysis of C_p vs T, to deduce a value for both $\nu_3(Ag)$ and the Debye frequencies, and of their temperature dependences (assumed to be linear as mentioned above (4)).

Assuming the contributions to C_p vs T due to the optic and to the acoustic modes are adequately accounted for by Einstein and Debye models (8), respectively, the temperature dependence of the specific heat may be written in the case of the α-phase in PDCB,

$$C_p = R\left[\underset{\substack{\text{internal}\\\text{optic}}}{\sum_{j=1}^{30}} \frac{x_j^2\, e^{x_j}}{(e^{x_j}-1)^2} + \frac{1}{2}\underset{\substack{\text{external}\\\text{optic}}}{\sum_{j=1}^{8}} \frac{1}{1-c_jT}\,\frac{x_j^2\, e^{x_j}}{(e^{x_j}-1)^2}\right.$$

$$+\frac{1}{2\,(1-c_3(Ag)T}\,\frac{x_3^2(Ag)\, e^{x_3(Ag)}}{(e^{x_3(Ag)}-1)^2}$$

$$\left.+\frac{9\,R}{(1-c_DT)}\,\frac{T^3}{T_D^3}\int_0^{T_D/T}\frac{x^4\, e^x}{(e^x-1)^2}\,dx\right] \tag{1}$$

where anharmonic perturbations on the normal mode frequencies have been taken into account (9) assuming the temperature dependence of the normal mode frequencies may be taken as linear, and that are written in the form $\nu_j=\nu_{oj}(1-c_jT)$; $x_j=h\nu_j/kT$, and the various symbols have their standard meaning (8), and the Debye temperature (T_D) is written as $T_D=T_{oD}(1-c_DT)$. The first term in the right-hand-side of Eq. 1 represents the contribution to the specific heat of the internal modes of vibration for the free molecule; the second term describes the contribution of the 8 known external optic normal mode frequencies; the third term corresponds to the unknown Ag rotatory optic mode; and the last term is that due to the acoustic modes.

The fitting of the parametres ν_{o3}(Ag), c_3(Ag), T_{oD}, and c_D in Eq. 1 to C_p vs T data is carried out following the least-squares procedure due to Deming (6). The values determined are: $\nu_3(Ag)=42.9(1-5.2*10^{-4}T)$, and $T_D(cm^{-1})=106.2(1-13*10^{-4}T)$, and when substituted into Eq. 1, the dotted curve depicted in Fig. 1 is obtained. As may be seen the description of the data is excellent. The value for T_D seems a reasonable one, unfortunately there are not other values to compare with; although it agrees well with the value of 110 cm^{-1} mentioned in Ref. 7, this agreement is fortuitous since the value deduced in Ref. 7 is meaningless. With respect to the value of ν_3(Ag) it may be said that, although there are not measured values to compare with, it is quite reasonable. Two pieces of information provide support to this statement. First, lattice dynamics model calculations (4) produce at 77 K the following values (in cm^{-1}): $\nu_1(Ag)=119$ (107), $\nu_1(Bg)=124$ (114), $\nu_2(Ag)=60$ (65), $\nu_2(Bg)=56$ (58), $\nu_3(Ag)=52$ (?), $\nu_3(Bg)=30$ (32). Bracketed values are experimental results (4), and the agreement obtained is qualitatively good and quantitatively reasonable. The value of 41 cm^{-1} determined in this work for ν_3(Ag) at 77 K agrees, within this frame of reference and the approximations involved, quite well with the calculated value of 52 cm^{-1} (4). The second piece of information is produced by analysing the temperature dependences of the 5 measured external rotatory modes. The slopes S are given by $S=\nu_oc$, and the values obtained are (in 10^{-2} cm^{-1} K^{-1}): $S_1(Ag)=5.8$, $S_1(Bg)=4.9$, $S_2(Ag)=5.4$, $S_2(Bg)=4.9$, and $S_3(Bg)=2.2$. As may be seen the S values for each pair of associated frequencies (rotatory modes about the same molecular axis but in-phase and out-of-phase) are quite close, therefore extrapolating this correlation a value near 2.2 would be expected for S_s(Ag). In fact this is the case, since S_s(Ag)=2.2, in complete agreement with our expectation.

ACKNOWLEDGEMENTS

Partial financial support provided by Consejo Nacional de Investigaciones Cientìficas y Tècnicas (CONICET) and by Consejo de Investigaciones Cientificas y Tecnològicas de la Provincia de Còrdoba (CONICOR), is gratefully acknowledged.

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