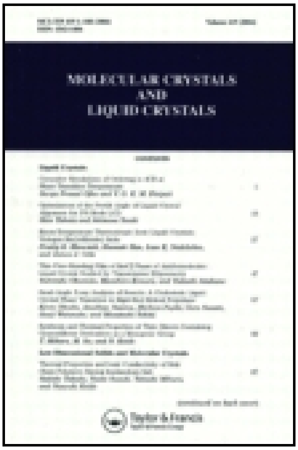

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P. Figuiere [a] & H. Szwarc [a]

[a] Laboratoire de Physico-Chimie des Rayonnemen ts(Associé au CNRS), Université de Paris-Sud, center d'Orsay, 91405, Orsay, France

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Raman Spectra in Molecular Solids: III. - Determination of the Phase Diagram of Solid P-Dichlorobenzene by high Pressure Raman Spectroscopy: Spoliation of the α-Phase[†]

P. FIGUIERE and H. SZWARC

Laboratoire de Physico-Chimie des Rayonnements(Associé au CNRS)
Université de Paris-Sud,
centre d'Orsay,
91405 Orsay France

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We have determined the phase diagram of solid p-dichlorobenzene by means of Raman spectroscopy up to five kilobars and we have shown that the triple point previously predicted between the three solid phases exists. The thermodynamical data for the different phase transitions are determined. We described a pressure treatment to get the equilibrium pressures at the transitions; this treatment shows that the "zone of indifference" can be diminished whereas the hysteresis range seems to be intrinsic to the solid sample. The explanation seems to lie in local stresses existing in the polycrystalline sample.

[†] : This work is part of P. Figuière's Thesis (Thèse de spécialité, Orsay 1973).

INTRODUCTION

In a former paper[1] we proved by Raman spectroscopy that in solid p-dichlorobenzene the γ phase, first observed by Dean and Lindstrand[2], was the true stable low temperature modification. Observations made by Kushida and Coll[3] by nuclear quadripolar resonance (N.Q.R.) led us to admit the existence of a triple point between the solid α, β and γ phases around room temperature and at a pressure of the order of 500. bars.

In order to prove this assumption we tried to determine the phase diagram of this compound by means of a volumetric method previously described[4]. Unfortunately the volume discontinuity at the $\alpha \rightleftharpoons \beta$ transition has a very weak value[5,6,7,8], so that we could not detect it. Furthermore such a low volume discontinuity also means that the slopes of the $\beta \rightleftharpoons \gamma$ transition curve and the corresponding $\alpha \rightleftharpoons \gamma$ curve are not very different and that the values for the $\alpha \rightleftharpoons \gamma$ and $\beta \rightleftharpoons \gamma$ volume discontinuities are approximately the same. As the transitions are very sluggish and the hysteresis effects have a great amplitude, we had no way with such a method to know whether the observed transitions were the $\alpha \rightleftharpoons \gamma$ or the $\beta \rightleftharpoons \gamma$ one.

As we knew that the Raman low frequency spectra corresponding to the three solid modifications of p-dichlorobenzene are quite different[1] we decided to observe these transition by Raman spectroscopy as a function of temperature and pressure. By this method we had no difficulties in identifying these phases and we could easily follow the phase transitions as they occured.

EXPERIMENTAL

The compound was obtained from commercial sources and was used without further purification.

Measurements of the Raman spectra were performed on a "PH 1 Coderg" double monochromator spectrometer. The samples were excited with a "spectra physics" 141 Argon Laser at 488 nm. The samples were placed within a high pressure Raman cell[†] which has been described elsewhere[9]. In this cell, the pressure which can be increased up to 12 kbars is measured by means of manganin coil surrounded by the liquid transmitting medium (petroleum ether) and the temperature, which can be varied from 200 to 450 K is known thanks to a thermocouple which was in contact with one of the optical windows. Furthermore, we are reasonably sure that the solid sample is submitted to hydrostatic pressures because the respective frequencies of the different external modes

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[†] : A.N.V.A.R. licence n° 71.661.00

attain the same values at a given point of the pressure-temperature diagram whether we operate at increasing or decreasing pressures, when that point is far enough from a transition line.

EXPERIMENTAL RESULTS AND DISCUSSION

a) *The phase diagram and related thermodynamical quantities*

The points on the transition lines were generally obtained by cycling the pressure up and down at a given temperature in a way analogous to the cycling of temperature by which we obtained the equilibrium temperature of the $\gamma \rightleftharpoons \alpha$ transition at atmospheric pressure[1]

This procedure was impossible to follow on the $\alpha \rightleftharpoons \beta$ transition line because the temperature range in which this curve exists is too tiny as we will see presently.

The equilibrium points we have detemined for the $\alpha \rightleftharpoons \gamma$ and $\beta \rightleftharpoons \gamma$ transitions have allowed us to draw the phase diagram of solid p-dichlorobenzene from 270 to 320 K up to 5 Kbars (Figure 1).

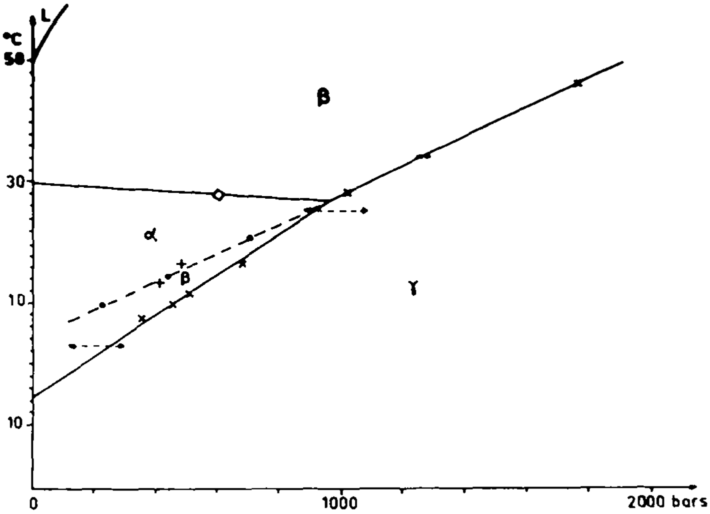

FIGURE 1 Phase diagram of solid p-dichlorobenzene

×	Equilibrium points determined by means of pressure cycling
←‑ ‑→	Hysteresis zone
•	Equilibrium points determined by volumetric measurements

On this diagram we can see that the $\beta \rightleftharpoons \gamma$ curve goes fair into the range of stability of the α phase. We can also see that the three transition points we have determined by volumetric measurements lie on that $\beta \rightleftharpoons \gamma$ line.

The fact that this line continues to exist in the α range has allowed us to determine the triple point with more accuracy by intersecting the $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \gamma$ curves. By joining this triple point and the point where phases α and β are in equilibrium at atmospheric pressure (304 K) with a straight line we could draw the $\alpha \rightleftharpoons \beta$ transition curve. This curve passes through the point where at 600 bars the α phase transformed into the β phase during an experiment in which we varied the temperature at a constant pressure.

It is surprising that the γ phase, which has long been considered as "anomalous", is the phase which in fact occupies the greatest range in the phase diagram whereas the α phase which was considered as being stable along almost the whole temperature range is restricted to such a small region.

The linear shape of the $\alpha \rightleftharpoons \gamma$ transition line contradicts the conclusion drawn by Balashov and Ikhenov[10] according which that curve should pass through a maximum. We have to notice that the way in which that conclusion was derived is a pure fallacy. They have drawn that curve from values of the $\alpha \to \gamma$ transition pressures they observed, at increasing pressures, at 273, 288 and 291 K and from the corresponding pressure value given by Kushida and coworkers[3] for an experiment made at 298 K. But it was already known that there is a strong hysteresis effect at that transition and of course we know that such effects are not reproductible from one sample to another and *a fortiori* from one author to another.

The triple point lies at 301 K and 980 bars. The fact that we previously underestimated the pressure value of that point[1] is due to the overshooting of the $\beta \rightleftharpoons \gamma$ transition line in the α stability range. Kushida and coworkers[3] had observed by N.Q.R. the $\gamma \rightleftharpoons \beta$ transition around 298 K when decreasing the pressure and that had led us to think that the β phase was still stable around this temperature value. We have to notice that it would have been almost impossible to draw the phase diagram from volumetric measurements because we would have been mistaken by the overshooting of the $\beta \rightleftharpoons \gamma$ transition curve.

The slopes of the three transition curves are given in the following Table (1)

TABLE I

Slopes of the three transition curves

transition curve	$\alpha \rightleftharpoons \beta$	$\beta \rightleftharpoons \gamma$	$\alpha \rightleftharpoons \gamma$
slope $\frac{dT}{dP}$ (K/bar)	– 0,003	0,022	0,032

TABLE II

Transitions / Thermodynamical values	$\alpha \leftrightharpoons \beta$	$\gamma \leftrightharpoons \beta$	o $\gamma \leftrightharpoons \alpha$
$\Delta V/V$	$-7{,}4 \,.\, 10^{-4}$(*) $+\ 0{,}0055 \pm 0{,}02$(a) $+\ 0{,}04 \pm 0{,}01$(b) $-\ 10^{-3}$ (c) $+\ 1{,}4 \,.\, 10^{-3}$(d) $(1{,}5 \pm 1{,}5) . * . 10^{-2}$(f)	$0{,}015 - 0{,}020$(*)	$0{,}015 - 0{,}020$(*) $-\ 5\% \pm 3\%$ (b)
ΔH(cal/mole)	176(*) 27,6 (d) 420 ± 140(e)	440 - 570(*)	280 - 380(*)
ΔS (e.u)	0,58(*) 0,091(*) 1,37(e)	1,56 - 2,08(*)	1,06 - 1,42(*)

(*) This work; *a*) Ref. 11, 12, 13; *b*) Ref. 7; *d*) Ref. 8; *e*) Ref. 6; *f*) Ref. 14.

From these experimental data and the approximative value for the volume discontinuity we determined by volumetric measurements at the $\beta \rightleftharpoons \gamma$ transition $(2.10^{-2} > (\frac{\Delta V}{V})_{\beta \rightleftharpoons \gamma} > 1{,}5.10^{-2})$ we have calculated values for the discontinuities of the different thermodynamical functions for the three observed transitions.

All the thermodynamical values we have determined are reported in table II in which we also wrote corresponding values given by others.

To calculate the different values corresponding to the $\alpha \rightleftharpoons \gamma$ transition we have admitted that the $\frac{\Delta V}{V}$ at the $\alpha \rightleftharpoons \gamma$ and $\beta \rightleftharpoons \gamma$ transitions are approximatively the same. This is justified by the fact that $\frac{\Delta V}{V}$ at the $\alpha \rightleftharpoons \beta$ transition is of the order of 10^{-3} as we will see later.

To give approximative values corresponding to the $\alpha \rightleftharpoons \beta$ transition we have assumed that the variations of the different thermodynamical discontinuities along the $\alpha \rightleftharpoons \beta$ curve are quite negligible between the triple point and the atmospheric pressure. Writing that

$$\Delta S_{\alpha \to \beta} + \Delta S_{\beta \to \gamma} + \Delta S_{\gamma \to \alpha} = 0$$

around the triple point, we get for the variation of entropy at the $\alpha \rightleftharpoons \beta$ transition:

$$\Delta S_{\alpha \to \beta} \simeq 0{,}58 \text{ e.u}$$

Then the Clapeyron formula gives:

$$\left(\frac{\Delta V}{V}\right)_{\alpha \to \beta} = -7.10^{-4}$$

This low value is in good agreement with the fact that Ueberreiter[5] could not detect that transition by means of volume measurements. It is also in good agreement with crystallographic data†[11, 12, 13] and with the values we can work out by applying the Clapeyron formula to the thermal data given by Kozhin et al.[8] and by Walsh and Smith.[6] We find:

$$\left(\frac{\Delta V}{V}\right)_{\alpha \to \beta} = -1{,}2.10^{-4} \quad \text{(from Kozhin's results)}$$

$$\left(\frac{\Delta V}{V}\right)_{\alpha \to \beta} = -1{,}7.10^{-3} \quad \text{(from Walsh and Smith's results)}$$

We have to notice that this last value is certainly too high because Walsh and Smith have ajusted the value of $\Delta S_{\alpha \to \beta}$, derived from sublimation experiments so that

$$\Delta S_{\alpha \to \beta} = R \text{ Ln } 2$$

All these results justify the approximation we made according which:

$$\left(\frac{\Delta V}{V}\right)_{\alpha \to \gamma} \simeq \left(\frac{\Delta V}{V}\right)_{\beta \to \gamma}$$

b) Determination of the equilibrium transition points: pressure cycling in relation to hysteresis effects and the "indifference zone"

As we said before, in order to determine the equilibrium points on the different transition lines with the best possible accuracy, we have been led to apply a special pressure treatment to the solid samples, by cycling the pressure up and down isothermally around the transition pressure. For instance let us examine the experimental procedure at 290 K. Starting with the pure γ phase at 830 bars we decrease the pressure step by step. At every step a Raman spectrum is

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† The agreement with results obtained by neutron scattering measurements (14) seems poorer but these later measurements agree with Jeffrey and McVeagh's radiocrystallographic determination for the β phase structure (15) which has not been confirmed since (see next paper).

recorded in order to check whether the waited for transition to the α phase has already occured. At 220 bars the low frequency Raman spectrum shows the emergence of caracteristic lines of the α phase and a slight decrease of the intensities of the γ phase intermolecular lines which proves that the γ phase begins to transform into the α phase. At that point, in order to keep the two phases in coexistence the pressure is increased some 50 or 60 bars. At this pressure value Raman spectra are recorded at regular time intervals and no evolution of the system is observed even for times as long as three hours. We must notice here that an evolution of the equilibrium between the γ and α phases should be easily detected in our experimental conditions because in the spectrum of the γ phase, the 50 cm $^{-1}$ line is very sharp and intense and the intensity of this line is very sensitive to any variation of the γ phase concentration.

Now we go on increasing the pressure step by step, checking at every step that there is no evolution of the binary phase mixture, up to 750 bars where the intensity of the γ 50 cm $^{-1}$ line begins to increase and some lines of the α phase spectrum begin to decrease. At this moment the pressure is decreased some 50 bars. We follow the same procedure as before observing again the non-evolution of the system down to 300 bars where the α phase begins to grow again. We can notice that this pressure value is higher than the value where the α phase began to grow from the pure γ phase.

Cycling the pressure over and over again in the same way allowed us to shorten the pressure range inside which we could not observe any evolution of the binary mixture down to the ultimate discrimination of our pressure measurement (≃20 bars). Such a pressure treatment is presented on figure 2. If, at any cycle, we let one phase transform entirely into the other, it is necessary to go

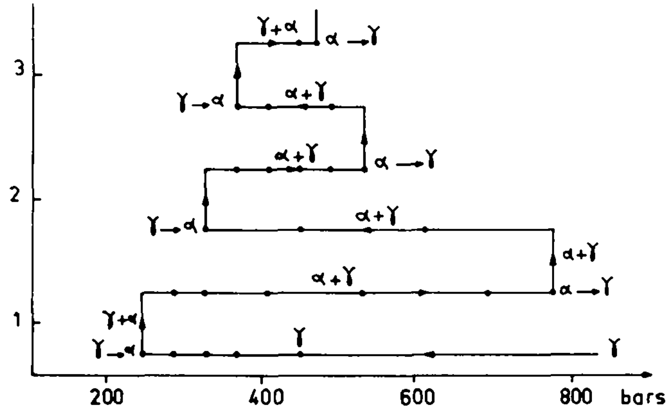

FIGURE 2 Pressure cycling procedure at 290 K.

through the whole procedure again, getting the same pressure value for the emergence of the α phase from the pure γ phase i.e. 220 bars at 290 K.

The range of pressure in which the binary mixture does not evoluate has been called "zone of indifference" by P. W. Bridgman[16] .

According the experiments we just described it seems that in the case of p-dichlorobenzene, it is possible to reduce that "zone of indifference" by an adequate pressure treatment. On the contrary, it appears that the hysteresis range limited by the pressure values at which one phase appears from the other pure phase at increasing pressures, is intrinsic for a given sample and does not seem to depend on former treatments.

c) Discussion. A possible origin for the "zone of indifference": local stresses

During the previous experiments we have followed the isothermal pressure shifts of the low frequency Raman modes. We shall only describe here a phenomenon which seems related to what we just described.

We have already said that the measured frequency of a given mode at a given point in the P – T diagram does not depend on the thermodynamical path

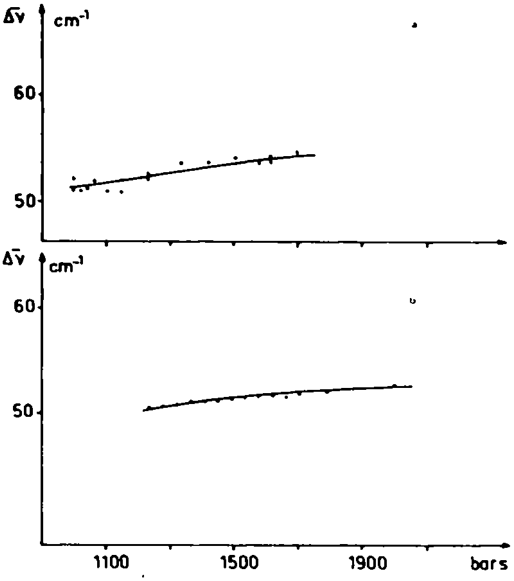

FIGURE 3 The effect of pressure treatment on the frequency shifts of the Raman mode lying near 50 cm^{-1}
a) when the pressure cycling is applied at 302 K
b) when decreasing the pressure in a monotonous way at 308 K.

followed to reach these conditions as far as this point is far enough from a transition line. But in the vicinity of a transition curve, a dispersion in the frequency values may be observed. This phenomenon is enhanced by the pressure cycling treatment.

Figure 3 shows the difference between the pressure frequency shifts of the 50 cm $^{-1}$ line in the γ phase spectrum obtained at 308 K when decreasing the pressure in a monotonous way (Figure 3b) and at 302 K when cycling the pressure (Figure 3a). We can see that in the former case the experimental points lie on a smooth curve, but that they present an important dispersion in the later case. This dispersion which can reach 2 cm $^{-1}$ and more cannot be explained by experimental errors (because the 50 cm $^{-1}$ line is quite narrow and intense) or by an overall pressure gradient inside the sample than the extent of the pressure range explored during the cycling.

So we must conclude that this frequency dispersion is probably due to local stresses which appear in the solid polycrystalline sample around the solid-solid phase transition.

This conclusion is supported by the fact that a monocrystalline sample of the α phase easily transforms into the γ phase during a slight cooling under 272 K,[17] which is very difficult in the case of a polycrystalline sample and has only been observed by Gash et al.[18]

Acknowledgement

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