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Raman Spectra in Molecular Solids II. Low Frequency Raman Spectroscopy as a Means to Study Phase Changes: More about the "Anomalous" γ-Phase of *p*-Dichlorobenzene

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Abstract—The temperature dependence of the Raman low frequency spectra of the three solid polymorphic phases of *p*-dichlorobenzene has allowed us to prove that the so-called "anomalous" γ-phase is, in fact, the actual stable low temperature modification (below 279 K): we have shown that the transformation (α, γ) is reversible at atmospheric pressure.

Our results and previous ones obtained under pressure by others lead us to deduce the existence of a triple point between the three solid phases of *p*-dichlorobenzene around room temperature and at pressures of the order of 500 bars.

Paradichlorobenzene is known to have three solid modifications: a high temperature triclinic phase (β)(1,2,3) existing between 304 K and the melting point at 326 K, a low temperature monoclinic phase (α)(2,3) existing below 304 K and a so-called "anomalous" phase (γ) which can exist at low temperatures. This γ phase was first observed by NQR by Dean and Lindstrand(4) as a transient low temperature phase and was then studied by others(5,6,7) with the same technique. The low frequency Raman spectra of phases α and β are well-known(8,9,10) and the different modes have been assigned thanks to measurements on monocrystals.(11,12,13) The Raman spectrum recently assigned to the γ-phase(14) is, in fact, the low temperature quenched β-phase spectrum (as we shall see further). Until now, this γ-phase was considered as a low temperature "metastable" modification as compared to the α phase, but it was proved(6,7) to be stable between 273 and 300 K at pressures of the order of 1000 to 2000 bars.

We were studying the temperature shifts of the low frequency Raman modes of the α and β phases, when we encountered the γ-phase and we have been able to determine its range of existence. Our experimental technique has been described in details before.(15)

Starting from the melt, the temperature was rapidly decreased to 108K. At this temperature, we observed the Raman spectrum of the quenched β phase (Fig. 1a). Then, we slowly warmed the sample in order to follow the shifts of the different low frequency modes up to the expected transformation into the α phase. This procedure enabled us to be sure that the spectrum represented on Fig. 1a corresponds to phase β because the temperature shift curves of its three lines extrapolate to the curves corresponding to the β-phase

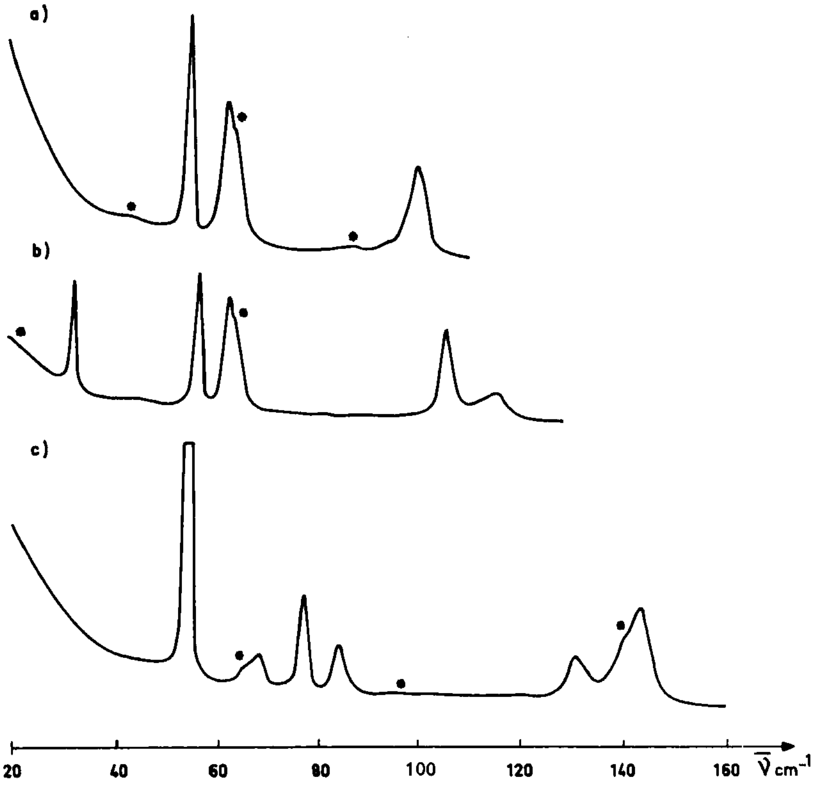

Figure 1. Raman low frequency spectra of *p*-dichlorobenzene at 108 K. (a) trapped β phase; (b) trapped α phase; (c) γ phase.

* Grating ghosts.

spectrum in its range of stability, i.e. between 304 K and the melting point.

Around 240 K, there was indeed a modification, but the spectrum we observed then was not that of the α phase. It certainly corresponds to the " anomalous " γ-phase of Dean and Lindstrand because, on warming, we saw its spectrum disappear around 278–280 K (as was observed for the γ-phase by Buyle-Bodin(6)) to give the α phase spectrum which can be easily identified. If, instead of warming the γ-phase, we decreased the temperature to 108 K, we found the spectrum of Fig. 1c which indicates that phase γ can be cooled down. From this point, we could increase the temperature to follow the shifts of its lines up to the transformation into the monoclinic α phase around 278 K.

Of course, there was no problem in cooling this last phase to 108 K, in observing its spectrum (Fig. 1b), then in following the temperature shifts of its lines up to 304 K, where we got the high temperature triclinic β-phase spectrum we followed up to the melting point.

We had now the spectra of all three phases at 108 °K and we could compare them. If we suppose, as a work hypothesis, that the respective lines of the spectra of phases α and γ correspond to similar modes, it is striking that the γ-phase lines lie at higher frequencies than those observed in the spectrum of the α phase which was supposed to be the stable low temperature phase. This would indicate a closer packing in phase γ than in phase α, which of course is consistent with the fact that phase γ is a high pressure modification. But this led us to assume that phase γ was the actual stable low temperature phase at atmospheric pressure.

In order to prove this assumption, we warmed the γ-phase up to the temperature where it begins to transform into the α phase and we set to observe the most intense line of the γ-phase spectrum (that is the line which lies around 45 cm^{-1} at 275 K). At 279.5 K, the intensity of the observed line showed a strong decrease and Fig. 2a shows the 45 cm^{-1} line and a 50 cm^{-1} one which reveals the presence of phase α in the sample. At that moment, we knew that phases α and γ coexisted within the sample. So, we cooled slightly to 270–271 K and we observed the spontaneous evolution of the two lines at a constant temperature as function of time. This evolution is represented on Fig. 2, on which we can see that the 45 cm^{-1} line increases steadily with time, whereas the 50 cm^{-1} line decreases. After 30 minutes, only the γ-phase line was left. If phase γ had been metastable as compared to α, a slight cooling could not have affected the $\gamma \rightarrow \alpha$ transformation which had begun and we should have got the α phase spectrum instead. So, this was the indisputable proof

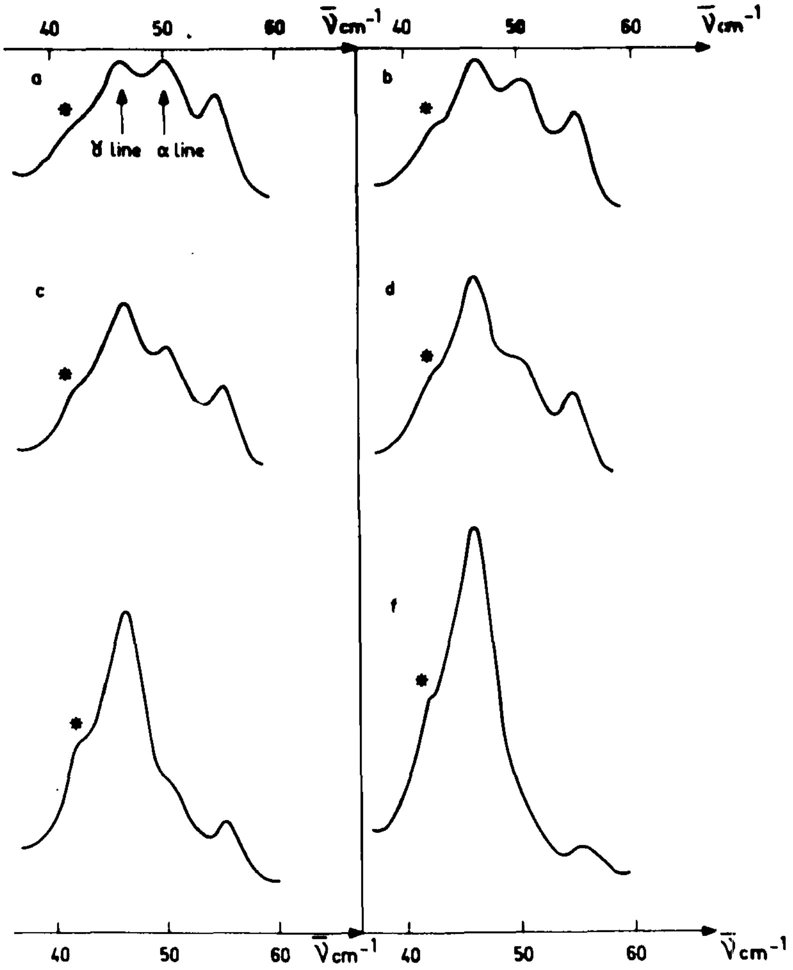

Figure 2. Spontaneous evolution vs. time of the low frequency Raman spectrum of the coexistent α and γ phases of p-dichlorobenzene in the 50 cm^{-1} region at 270 K. (a) $t = 0$; (b) $t = 25$ sec; (c) $t = 2$ mn 50 sec; (d) $t = 7$ mn 50 sec; (e) $t = 20$ mn; (f) $t = 30$ mn 05 sec.

* Grating ghost.

we were looking for that phase γ is the true stable low temperature phase.

Now, we can describe the stability ranges of the three solid phases of *p*-dichlorobenzene as follows:

T(K)		279		304		326
Phases	γ	$\gamma \rightleftarrows \alpha$	α	$\alpha \rightleftarrows \beta$	β	$\beta \rightleftarrows$ liquid

Furthermore, Kushida and coworkers(6) have shown that, around room temperature, phase α transforms into phase γ at 1600 bars at increasing pressures, and that, around 750 bars, phase γ transforms into phase β when the pressure is decreased. Knowing that phase γ is a stable modification at atmospheric pressure, we now can conclude that there is, in the phase diagram of *p*-dichlorobenzene, a triple point between the three phases, α, β and γ, around room temperature and at a pressure of the order of 500 bars. The existence of such a triple point could explain the sluggishness of the different phase transitions at atmospheric pressure when the temperature is decreased and the corresponding impossibility to get phase γ from a pure α phase under the same conditions, because, according to Bridgman(16), there often is a "zone of indifference " around a solid-solid transition curve and that this phenomenon is probably enhanced by the vicinity of a triple point: so, the (pure α) $\rightarrow \gamma$ transition would be too slow to be observed.

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