

FIR-Spectroscopy in the High Pressure Phase of Polyethylene

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Summary

Despite the experimental problems of the high pressure and the high temperature necessary to reach the hexagonal phase of polyethylene a new absorption band was discovered and ascribed to a lattice vibration of this phase. This implies a well ordered lattice over considerable distances. From the frequency which lies between the frequencies of the B_{1u} - and B_{2u} -lattice vibrations of the orthorhombic crystal it is deduced that the hexagonal phase consists mainly of helical sequences and that the lattice vibrations do contribute little to the entropy difference orthorhombic hexagonal.

Introduction

High pressure Far Infrared Spectroscopy on polyethylene has been shown to be a powerful tool to probe the intermolecular interactions within the crystalline phase. At room temperature, the frequency of the translational B_{1u} -lattice vibration has been measured up to 7 kbar (LEUTE & FRANK 1980), the anharmonicity of this vibration has been studied and potential functions have been tested by the comparison of a calculated pressure dependence of the frequency with the experimental one (LEUTE & GROSSMANN 1981). At moderately elevated temperature, a step has been observed in the curves frequency vs temperature measured at sufficiently high pressure which has been discussed in terms of a relaxation process or of a phase transition - the former has to be ruled out (LEUTE 1981).

Obviously, it is tempting to measure also at a considerably higher temperature and at more than 3.5 kbar in order to reach the high pressure phase of polyethylene (BASSETT & TURNER 1972, LEUTE & DOLLHOPF 1980). The extraordinary importance of this phase lies in the fact, that with respect to entropy, enthalpy, volume,

Raman spectra and shear modulus it is quite close to the melt and consequently 'reflects the structure of the melt' (YAMAMOTO 1979), at least under high pressure. On the other hand, YAMAMOTO reports three sharp equatorial Bragg reflections, 100, 110 and 200, so that the packing of parallel chains in the hexagonal lattice has to be rather perfect. Thus, parallelism - which means bundles (BLASENBREY & PECHHOLD 1970, PECHHOLD 1980) - might be encountered in the melt, too.

However, before entering this field of conclusions, one should make certain that the hexagonal phase itself is fully understood which is by no means the case. Hitherto it has been investigated with six experimental techniques - calorimetry, dilatometry, WAXS, ultrasonics, Raman spectroscopy and microscopy - but with the exception of X-ray scattering the methods do more reveal the melt-like character of the phase and not its crystalline aspects. It therefore seems desirable to add experimental evidence to the characterization of order in the phase which is done in the present paper by seeking a lattice vibration. This should also further the understanding of its entropy and - together with the result of all other techniques and of atomistic potential calculations - of its structure.

Experimental

The apparatus described earlier (LEUTE & FRANK 1980) had to be modified. The temperature of the high pressure optical cell exceeds 500 K which means strong infrared radiation by the oxidized steel. The light pipe itself does not disturb since it is cooled, but it collects the radiation from an area comprising more than 99% steel surface, only the remainder is window surface through which the chopped beam from the lamp can come. Usually only chopped

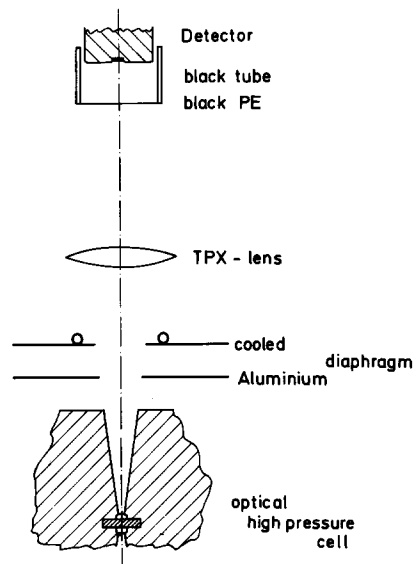


fig. 1:
Optical system for high temperature measurements replacing the light pipe

light is registered, but here the Golay Detector was clearly overloaded, it became extremely sensitive to microphony and interferograms consisted of little more than noise.

Although the lightpipe was effective and convenient at moderate temperature, it had to be replaced by the optical system in fig. 1. This needs good adjustment, but it focusses only light from the sample onto the detector. Stray light and draught from the hot cell are kept off by the closed black cylinder, unwanted radiation is reduced by the reflecting and the cooled diaphragms, and poly(4-methylpentene-1) (TPX) is a reasonable lens material in the FIR spectral range (SMITH & LOEWENSTEIN 1975).

Results and Discussion

Somewhat above 200°C and at a pressure of 4.5 kbar the frequency of the B_{1U} -lattice vibration of the orthorhombic crystal is about 80 cm^{-1} (LEUTE 1981). The spectrum in fig. 2 which has been measured at 237°C shows despite the noise a strong absorption band

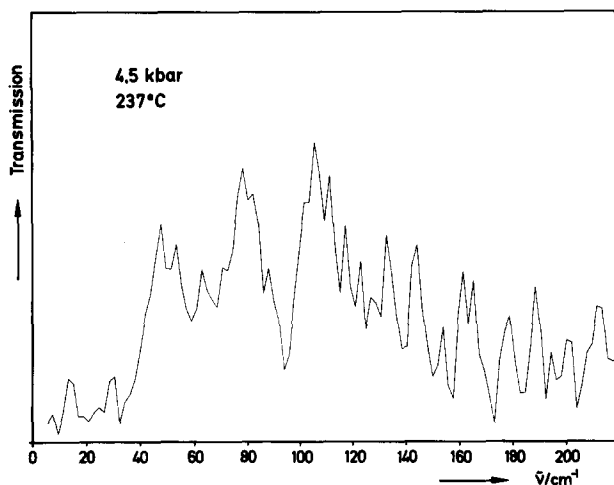


fig. 2: Spectrum of polyethylene in the hexagonal phase. No background has been subtracted.

at 93.5 cm^{-1} , approximately. Its great distance from the 'orthorhombic' vibration can be seen in fig. 3.

With the very same experimental set-up spectra have been measured at room temperature without pressure and at 170°C at 4.5 kbar (where even more pressure transmitting silicone oil is in the light beam). Always only the B_{1U} -lattice vibration was found at

the right position. Swelling - though improbable - or the beginning of melting would rather decrease the frequency.

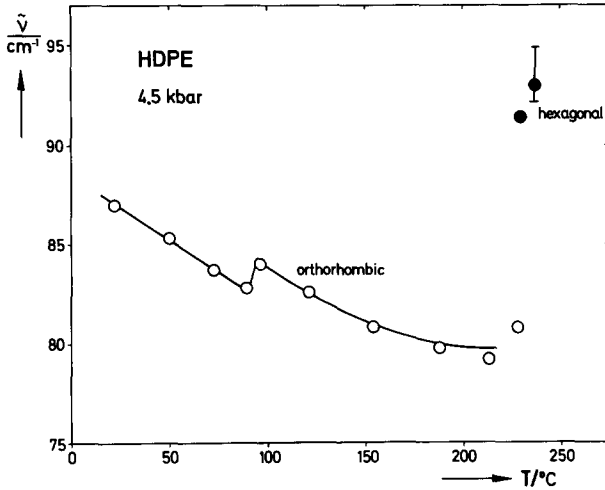


fig. 3: Frequency of the observed absorption bands of polyethylene at 4.5 kbar as a function of temperature

Lamellar thickening by annealing should not affect the frequency since it is the same for extended chain material and samples crystallized at atmospheric pressure if measured at room temperature (FRANK et al. 1981).

There remains the explanation, that the new band is to be ascribed to a lattice vibration of the hexagonal phase.

One might object that the lowest temperature where the 'hexagonal' band has been observed is hardly 230°C (see fig. 3) which does not exactly fit the phase diagram (LEUTE & DOLLHOPF 1980). However, the molecular weight of the material used in the present studies is comparably small, (30 000, see also LEUTE 1981) which lowers the transition temperature (BASSETT 1976); in addition, the point was determined from a sample with a density of only 0.973 g/cm³ whereas the phase diagram is given for extended chain material. The dilatometric curve of this sample began to ascend towards the transition below 220°C.

For the sake of transparency not all data points of the

'hexagonal' bands are shown in fig. 3. Comparing all measurements we find, firstly, that samples of low density (0.973 g/cm^3) seem to have a lower frequency ($89\text{-}91 \text{ cm}^{-1}$) than samples which were crystallized from the high pressure phase ($93\text{-}95 \text{ cm}^{-1}$). Secondly, for a given type of sample, the frequency seems to decrease with increasing temperature, as it can be expected. Unfortunately the temperature variation had to be small, for the signal to noise ratio deteriorates strongly with increasing temperature. This made it impossible to measure at a clearly higher temperature and pressure where the phase is more extended in the phase diagram, and to study there the pressure and the temperature dependence of the vibration. The noise and hence the experimental uncertainty are bad enough at 4.5 kbar and about 230°C .

To every vibration an entropy is to be attributed. The vibrational entropy of one oscillator with the frequency ω at the temperature T is given as

$$S_{\text{vib}} = k \left\{ \frac{\frac{\hbar\omega}{kT}}{e^{\frac{\hbar\omega}{kT}} - 1} - \ln \left(1 - e^{-\frac{\hbar\omega}{kT}} \right) \right\}$$

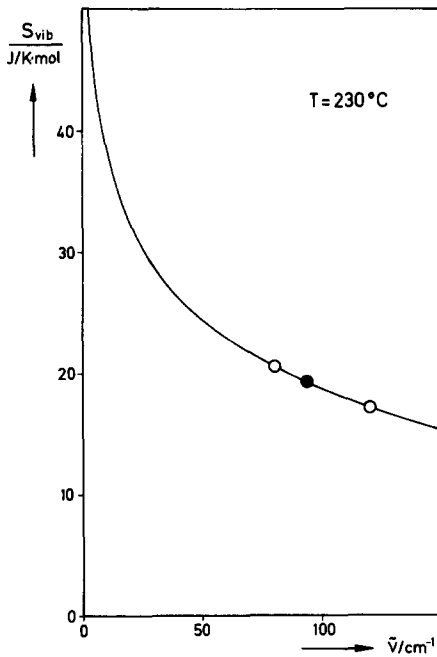
where k denotes Boltzmann's and \hbar Planck's constant.

For a mole oscillator and 230°C the function is shown in fig. 4. The entropy corresponding to 93.5 cm^{-1} (filled circle, 'hexagonal' band) is $19.3 \text{ J/K} \cdot \text{mole}$, to 80 cm^{-1} belongs $20.6 \text{ J/K} \cdot \text{mole}$ (left empty circle, B_{1u} 'orthorhombic' band). Thus we have an entropy difference

$$\Delta S_{\text{vib}} (80 - 93.5) = -1.3 \text{ J/K} \cdot \text{mole}$$

The frequency of the B_{2u} -lattice vibration of the orthorhombic crystal can be roughly estimated from its temperature dependence (FRANK et al. 1977) and the pressure dependence of the B_{1u} -vibration (LEUTE & FRANK 1980) corrected with the smaller compression of the b -axis (ITO 1979), which gives 120 cm^{-1} (right empty circle). This yields an entropy of $17.2 \text{ J/K} \cdot \text{mole}$ and a difference of

$$\Delta S_{\text{vib}} (120 - 93.5) = 2.1 \text{ J/K} \cdot \text{mole}$$



Summing up, we have an entropy difference due to the different frequencies of the lattice vibrations of less than 1 J/K·mole, whereas the total entropy difference between orthorhombic crystal and hexagonal phase amounts to about 7.5 J/K·mole (LEUTE & DOLLHOPF 1980).

fig. 4:
Vibrational entropy of an oscillator

Deductions

The very existence of a lattice vibration implies good lateral order in not too small regions. Improbable are therefore many big defect disturbing the lattice and great blocks out of two different kinds of conformations.

From the value of the frequency we can draw three important conclusions. Firstly, we have no frequency decrease compared to the B_{1U} -vibration as it could be expected from the increase in lattice dimensions at the transition. The conformation of the molecule in the hexagonal phase has to be laterally harder; this means - according to potential calculations by GROSSMANN (1977) - the $4 \times 1/1$ Helix which has already been proposed by PECHHOLD et al. in 1976. This helical conformation has to constitute the major part of the chain since it determines the lattice and its vibrational frequency.

Secondly, the contribution of the lattice vibration to the entropy difference orthorhombic crystal - hexagonal phase is small, less than 15%. This is by no means trivial, since a decrease of frequency

would have led to a very large portion. Since high frequency vibrations do not contribute (see fig. 4), almost the whole entropy difference has to be explained in terms of the structure of the chain (e.g. similar to PECHHOLD et al. 1976, GROSSMANN 1977). This had been assumed, but now the proof is given.

Thirdly, the position of the 'hexagonal' band between the two 'orthorhombic' ones implies that the bulk modulus should not change very much during the transition. This explains one result from the ultrasonic measurements (MATSUSHIGHE & TAKEMURA 1980). The shear modulus does not describe the lattice, its low value has to come from defects, dislocations, superstructural surfaces, small c-axis gliding etc.

If we take from the Raman spectroscopy the evidence that the hexagonal phase contains as many gauche bonds as the melt (TANAKA & TAKEMURA 1980, SCHWICKERT 1980) - which holds for the Helix - as well as some short trans-sequences of up to 4 CH₂ (SCHWICKERT 1980) we may deduce the following model: A chain consists of helical parts and perhaps 20 % trans-sequences as statistical defects. To avoid bends, these are out of 2 or 4 CH₂-groups. This complies with the c-axis data (YAMAMOTO 1979, LEUTE & DOLLHOPF 1980) and does not contradict any experimental finding. A more detailed analysis is to be given elsewhere.

Acknowledgements

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