

High Pressure FIR-Spectroscopy on Polyethylene at Elevated Temperature

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Summary

The temperature and pressure dependence of the translational B_{1u} -lattice vibration has been determined in the pressure range of 7 kbar and a temperature range of almost 200 K from room temperature upwards. For some pressure values the Grüneisen Parameter has been evaluated as a function of temperature. A detailed discussion is given for a step in the $\tilde{\nu}(T)$ -curves at elevated pressure.

Introduction

In the Far Infrared spectral range polyethylene has a very simple spectrum. If measured at atmospheric pressure and ambient temperature it consists only of one strong band at about 73 cm^{-1} which has been assigned to the translational lattice vibration of species B_{1u} . This is parallel to the b-axis of the orthorhombic unit cell and polarized in a-axis direction (TASUMI & SHIMANDUCHI 1965 and TASUMI & KRIMM 1967). The behaviour of this vibration has been studied either by the variation of temperature (FRANK et al. 1977 and KOBAYASHI & TADOKORO 1977) or by applying an external pressure of up to 7 kbar (LEUTE & FRANK 1980 and LEUTE & GROSSMANN 1981). By the latter method we were able to show that the frequency shift with pressure considerably exceeds the effect of the greatest temperature variation possible and follows at room temperature the equation:

$$\tilde{\nu}_{B_{1u}} = 73.1 \text{ cm}^{-1} + 3.59 \frac{\text{cm}^{-1}}{\text{kbar}} p - 0.094 \frac{\text{cm}^{-1}}{\text{kbar}^2} p^2$$

Furthermore, the Grüneisen Parameter of the B_{1u} -vibration have been evaluated including their pressure dependence and the experimentally established pressure dependence of the frequency has been calculated theoretically invoking semiempiric atomistic potentials.

In the preceding paper only the results of experiments carried out at room temperature were reported in

detail. Measurements at elevated temperature and their interpretation will be presented here.

Experimental particulars of High Pressure Far Infrared Spectroscopy have been described earlier (LEUTE & FRANK 1980). We shall only repeat the characterization of the sample material which has been Lupolen 6011L by BASF, a linear Polyethylene with a molecular weight $\bar{M}_n = 30\ 000$ and $\bar{M}_w/\bar{M}_n = 2$. Samples were prepared by melting the polymer under vacuum at 190°C with subsequent slow cooling under a pressure of 500 bar. The resulting density was $0.973\ \text{g/cm}^3$ and corresponds to a crystallinity of 83 %.

Results

When the frequency of the B_{1U} -lattice vibration of polyethylene is plotted versus pressure for several temperatures a set of nearly parallel curves is found (fig. 1).

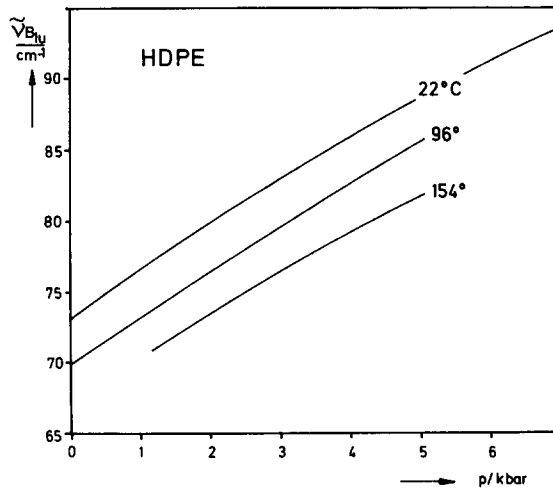


fig.1: Frequency of the B_{1U} -lattice vibration versus pressure for a few selected temperature values

Small deviations from parallelism can be expected since with increasing temperature the signal to noise ratio deteriorates and the data points scatter. However, when scrutinizing the curves measured at temperature values near 90°C we found that they would intersect at a pressure somewhere below 3 kbar. The effect becomes much more transparent when the points are drawn in a diagram frequency versus temperature with the pressure as parameter as it has been done in the upper part of fig.2. Between 90°C and 95°C a sharp

step upwards occurs in the otherwise slowly declining curves. Since the step is of nearly the same height as the experimental error - at least for 3 kbar - we wanted to correlate the effect with findings from independent methods: By the use of a high pressure X-ray camera NAKAFUKU (1978) obtains steps in the lattice dimensions of polyethylene at exactly the same temperature. His data on the a-axis where the step can be seen most clearly is therefore included in fig. 2 (NAKAFUKU has measured at 3 and 4 kbar, the curve for 4.5 kbar has been extrapolated). At atmospheric

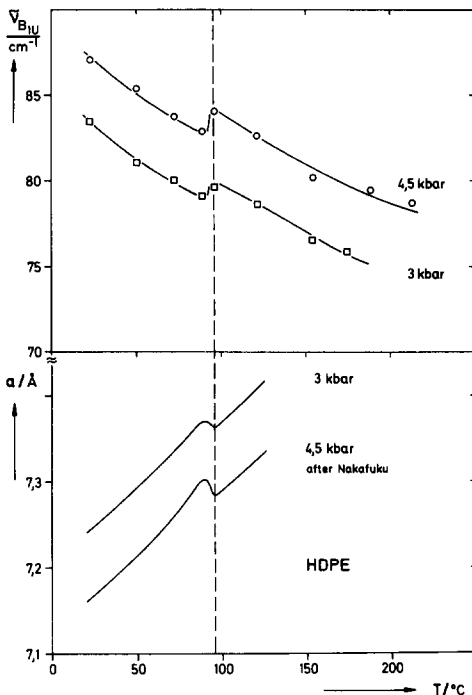


fig.2: Frequency of the B_{1U} -lattice vibration versus temperature for two pressure values

result is plotted in fig. 3 and shows the decrease of step height with decreasing pressure; below 2 kbar the step is hardly detectable.

We now invoke the volume data to evaluate the Grüneisen Parameter of the B_{1U} -lattice vibration from its temperature dependence reported in fig. 2.

pressure or at rather low pressure no such steps have been observed. The step in the a-axis and the much smaller step in the b-axis yield of course also a step in a plot of the specific volume vs pressure. This is not given explicitly in NAKAFUKU'S paper, but it can be obtained in the following manner: NAKAFUKU gives formulae of the relative volume change due to pressure for a set of temperature values between 20°C and 130°C. After calculating the volume at 1bar and such a temperature according to SWAN (1962) that volume change has to be subtracted. The

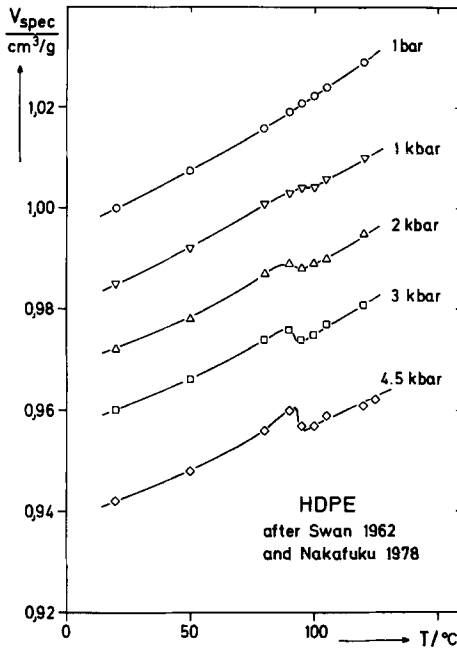


fig. 3:
Specific volume of
the polyethylene
crystal as a
function of
temperature for
some pressure
values, calculated
from data by SWAN
(1962) and NAKAFUKU
(1978)

It may be calculated from the equation (LEUTE & GROSSMANN 1981)

$$\gamma_V^{B_{1u}} = - \frac{d \ln \tilde{v}_{B_{1u}}}{d \ln V} = - \frac{V}{\tilde{v}_{B_{1u}}} \frac{d \tilde{v}_{B_{1u}} / dT}{dV/dT}$$

and can be seen in fig. 4 as a function of temperature for three pressure values; the points at atmospheric pressure are evaluated from data by FRANK et al. (1977). Since the above formula contains two derivatives - $d\tilde{v}/dT$ is particularly critical as can be seen from fig. 2 - the scattering of points is not unexpected. The value of the Grüneisen Parameter decreases with temperature, much more at high pressure than at 1 bar but near 90°C a minimum is passed with subsequent temperature independence or even increase with temperature.

Discussion

Literature data on $\gamma(T,p)$ are scarce and controversial. The temperature dependence of the Grüneisen Parameter given in fig. 4 for atmospheric pressure is in fair agreement with the curve given by NAKAFUKU (1978). A diagram γ versus T is also given by KIJIMA (KIJIMA et al. 1965 and KIJIMA et al. 1976)

containing curves measured at 0, 1 and 2 kbar with an ultrasonic technique on single crystal mats. As discussed earlier (LEUTE & GROSSMANN 1981) those results deviate considerably from the data obtained with most other methods and their temperature dependence, too, goes in the opposite direction. We have to mention, however, that also a theoretical Grüneisen Parameter calculated by BROADHURST and MOPSIK (1971) increases with increasing temperature.

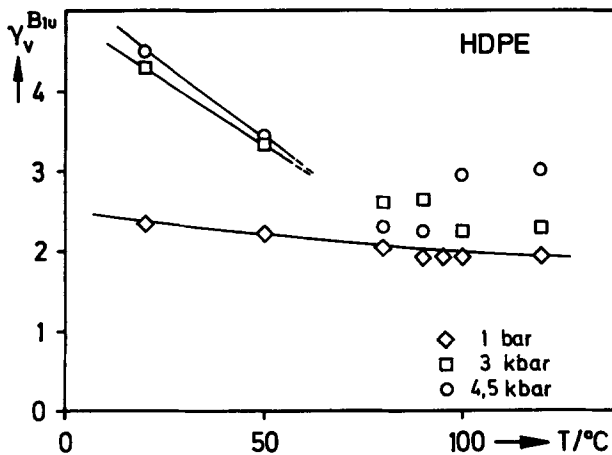


fig. 4: Grüneisen Parameter of the B_{1U} -lattice vibration as a function of temperature for three pressure values

The above authors (KIJIMA et al. 1976) find for extended chain material almost no temperature dependence at 1 bar which fits better our result. There seems to be a strong influence of sample preparation and method of determination which renders comparison difficult. (The small difference between the parameter values at 20°C in fig. 4 and our earlier $\gamma(p)$ curve (LEUTE & GROSSMANN 1981) can be explained by the fact that then we used the fitted parabola $\tilde{\nu}(p)$ for evaluation and at present directly the points and slopes in fig. 2).

What can be clearly seen from fig. 4 and literature is, that something happens near 95°C. This is of course the step in lattice dimensions at this temperature which can be detected by X-ray or by a method particularly sensible to variations of the a-axis - the latter is the observation of the translational B_{1U} -vibration as we have shown elsewhere (LEUTE & GROSSMANN 1981). The question arises

why it has not been seen in high pressure dilatometry (e.g. DOLLHOPF et al. 1980). Its is probably because the step is of the order of 0.5 % and is further reduced and smeared out due to the amorphous phase in partially crystalline samples. Extended chain material on the other hand shows the step much less than a sample drawn and annealed (NAGAFUKU 1978). Only for branched polyethylene a slight deviation from the usual smooth curves is found in the temperature range of interest which might have to do with our findings (DOLLHOPF 1979).

There remains to be discussed which molecular process causes the phenomenon. According to NAKAFUKU the step in the curve a-axis vs temperature observed at high pressure "seems to be concerned with the crystalline dispersion of PE" (NAGAFUKU 1978). In particular, the α_2 -relaxation¹⁾ has been reported to be located at 96°C by KIJIMA et al. (1974).

In order to appraise the assignment of the steps in figs. 2 and 3 to the α_2 -relaxation we have to look at an activation diagram (MÜLLER et al. 1975) for 1 bar. Spectroscopy and X-rays observe in a static experiment, i.e. at a frequency of 10^{-3} Hz or below which fits very nicely a temperature of 96°C for the α_2 -process. KIJIMA et al. (1974), on the other hand, use longitudinal sound waves of 4.64 MHz, plot the sound velocity vs temperature and find a step at 96°C. According to the activation diagram that high frequency corresponds to about 660°C for the α_2 -process so that it can be either the β -process or the method yields actually 'static' values, too. This might be explained, if we visualize that the sound velocity is $\sqrt{E \cdot V}$ where E denotes the modulus which strongly decreases with temperature.

¹⁾ There are various molecular explanations for the mechanical α -processes given in the literature (e.g. TAKANAYAGI 1965, SINNOT, 1966, MCCRUM & MORRIS 1966) PECHHOLD and coworkers describe them in terms of the meander model (MÜLLER et al. 1975). In this model the α_2 -process is a cooperative c-axis shear deformation of half meanders. A defect (e.g. jog) migrates along one chain across the lamella which results in a screw dislocation with burgers vector c. The same happening in adjacent chains causes diffusion of the screw dislocation through the lamella. This is the elementary process of α_2 -deformation.

If this occurs monotonously the step in V causes a step in the sound velocity. Only, it is hard to understand why a volume change should not influence the modulus. Thus, based on relaxation data at 1 bar, our steps might have to do with the α_2 -relaxation, but it is difficult to assess the findings from ultrasonics for which the same mechanism is claimed.

The behaviour at elevated pressure, however, rises problems. From high pressure experiments invoking the ultrasonic technique (KIJIMA et al. 1974 and WADA et al. 1969), a torsion pendulum under gas pressure (PARRY & TABOR 1973) and the dielectric method (NAOKI et al. 1975 a,b,c and SAYRE et al. 1978), from samples out of single crystal mats and of bulk material, we know that all relaxation processes (α, β, γ) are shifted towards higher temperature with increasing pressure for a given frequency. No such pressure dependence can be found in figs. 2 and 3, hence we have to rule out that the steps in those figures are a direct consequence of the α_2 -relaxation.

If we assume instead a first order transition we find it reasonable that the step height increases with pressure, because the volume change is negative, similarly to a transition in PTFE (HIRAKAWA 1969). The very small pressure dependence of the transition temperature is unusual but not impossible. We know further, that the steps are more dominant for material with more amorphous content so that an interaction of the amorphous phase with the crystal has to be thought of, which gives rise to the transition with minute volume changes, detected in the crystalline region by our method. Still, the nature of the amorphous phase, particularly under high pressure, is by far not sufficiently known to go further in speculation.

Acknowledgments

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