On the pressure dependence and the Grüneisen parameters of the B_{1u}-lattice vibration in high density polyethylene

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Far infra-red spectroscopic measurements have been made on a high density (0.973 g cm^{-3}) sample of linear polyethylene to determine the frequency of the zone-centre B_{1u} translational lattice mode (vibrating in the *b*-axis direction) as a function of pressure up to 7 kbar. The variation of frequency over this range is found to exceed, considerably, its total variation with temperature up to the melting point. These measurements and X-ray data from the literature give a volumetric mode Grüneisen parameter $\gamma_V^{B_{1u}}$ varying from 3.15 at low pressures to about 5.5 at 7 kbar. Theoretical calculations using the potential functions of Hägele *et al.* give, for the special (anisotropic) Grüneisen mode parameters, $\gamma_a^{B_{1u}}=6.1$, $\gamma_b^{B_{1u}}=2.2$, and predict a pressure variation of $\tilde{\nu}$ (B_{1u}) similar to but greater than that observed experimentally. The results are compared with other data in the literature.

INTRODUCTION

In studying the interactions between polyethylene chains in the crystalline state, far infra-red spectroscopy is a most useful technique. In its frequency range those translational lattice vibrations which are active are perpendicular to the chain axis and therefore determined by the intermolecular force field alone[1,2], and they are the only bands in the spectrum. One band, the B_{2u}-vibration in *a*-axis direction[1,2] is detectable only at low temperatures[3] so that the present study shall deal with the B_{1u}-lattice vibration, parallel to the *b*-axis of the orthorhombic cell, polarized in the *a*-axis direction and located near 73 cm^{-1} at room temperature and atmospheric pressure[1,2].

In order to probe the intermolecular potential one may vary the intermolecular distances and observe the influence upon the band, in particular upon its frequency (for experimental reasons we cannot study line shapes etc. with sufficient accuracy). The lattice dimensions can be varied either by temperature or by pressure variation; the first method being relatively convenient has been applied by some workers[4,5] whereas the latter necessitates considerable experimental effort[6]. However, it seems worthwhile, because not only does the effect of several kbar exceed the effect of the maximum temperature variation between a few K and the melting point of polyethylene[4,6], but also $(\mathrm{d}\tilde{\nu}/\mathrm{d}V)_p$ and $(\mathrm{d}\tilde{\nu}/\mathrm{d}V)_T$ are fundamentally different properties (see below). Knowing the intermolecular potential one can calculate the equilibrium intermolecular distances and the frequencies of the two translational vibrations mentioned above (all for 0 K) and compare it with extrapolated experimental data[7]. If the calculated equilibrium lattice dimensions are not used, but X-ray values determined at various temperatures[8-10] are, then the temperature dependence of the frequencies may be calculated in the quasi-harmonic approximation which has been done, at least for the range 0–300 K[5,11-13]. Fortunately, wide angle X-ray studies have also been carried out at elevated pressure[14-18] which enables calculation of the potential as a function of pressure (see also ref. 15) and thence to derive the frequency of the B_{1u}-vibration and compare it with the experimental pressure dependence.

Important parameters depending on the anharmonicity of the intermolecular interactions are the mode Grüneisen parameters. The frequencies of truly harmonic vibrations do not depend upon lattice dimensions or volume so that the observed pressure (i.e. volume) dependence indicates deviation from harmonic behaviour. This is the first time, to our knowledge, that the Grüneisen parameter for a translational lattice vibration at room temperature has been evaluated directly from pressure experiments, only a librational vibration has been investigated similarly[19]. Furthermore, we shall determine the Grüneisen parameter not only in respect to volume change, but, invoking again potential calculations, the parameters in respect to the strains in the *a*- and *b*-axis directions. The results can be compared with findings obtained by the quite different method of temperature dependent Raman scattering[20].

Before reporting our results and discussing them we shall briefly describe our experimental and computational methods and outline some relevant aspects of the Grüneisen parameters.

BACKGROUND

Grüneisen parameters

Since there are numerous textbooks (e.g. references 21, 22) and original publications (e.g. references 20, 23–25) where derivations of the quasiharmonic Grüneisen theory are given in more or less detail, we shall restrict ourselves to the essential definitions and some remarks. Let $\varepsilon_i (i=a,b,c)$ be the strains in the directions of the three crystal axes:

$$\varepsilon_a=\frac{a-a_0}{a_0}\ ,\ \varepsilon_b=\frac{b-b_0}{b_0}\ ,\ \varepsilon_c=\frac{c-c_0}{c_0}$$

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then

$$\gamma_i^j = -\frac{\partial \ln \omega_j}{\partial \varepsilon_i}$$

is defined as the special or anisotropic Grüneisen parameter of the *j*-th normal mode with frequency ω_j in respect to the strain in *i*-direction.

The parameter describes the relative frequency change of a vibration when a strain in just one direction is applied. Clearly, in practice, this cannot be measured directly since stress in one direction causes a sample to be deformed in the other directions too (although for materials with strongly anisotropic thermal expansion such as paraffines it may be evaluated approximately[20]). Nevertheless it is of great interest in order to appraise mutual interaction of chains.

Measurable, and introduced by most theoretical treatments, is the 'Grüneisen parameter' of the *j*-th normal mode in respect to volume (*V*):

$$\gamma_V^j = -\frac{\partial \ln \omega_j}{\partial \ln V}$$

which relates a relative frequency change to a relative volume change under conditions of isotropic pressure. Subsequently we shall on occasion omit the subscript *V* ($\gamma_V^j = \gamma^j$).

If, by some experimental procedure, an average Grüneisen parameter $\bar{\gamma}$ is determined for a number of vibrations, this means an average in which the contribution of each normal mode is weighted by its contribution C_j to the specific heat C_V:

$$\bar{\gamma} = \sum_j \gamma^j C_j / \sum_j C_j$$

If all normal modes of the material are accounted for, the average is the quasi-harmonic expression for the thermodynamic Grüneisen parameter γ_{th}, the denominator of the above equation is C_V:

$$\gamma_{\text{th}} = \Sigma \gamma^j C_j / C_V = \frac{\alpha \cdot B \cdot V}{C_V}$$

Here *B* denotes the isothermal bulk modulus and α the coefficient of expansion.

Experiments yield either mode Grüneisen parameters (spectroscopy with variation of temperature or pressure) or some average. From X-ray scattering under pressure, for example, we expect an average of the translational lattice vibrations. More lattice vibrations (translations, librations) are probably measured by ultrasonic measurements (although no purely crystalline material is available, Wada[26] tried to eliminate the influence of the amorphous phase). Even more modes will be comprehended by bursts of MeV-electrons[27,28], a method not yet applied to polyethylene.

In order to allow the evaluation from a certain type of experiment, various equations have been derived from the exact definitions given above. Wu *et al.*[23] give as many as ten, most of them assuming some approximations. These and the type of averaging have to be taken into consideration when literature data are appraised. As already pointed out by Warfield[24] and Wada[26], often C_V is used when only the contribution of interchain vibrations to the specific heat should be taken. The latter amounts to only 10 or 20%[24] of the calorimetric value, so that the appropriate average exceeds γ_{th} by a factor of about 10. This is reasonable since almost harmonic high frequency vibrations contribute to γ_{th} having minute $\gamma^j (< 0.1)$[23,29].

So far we have discussed the Grüneisen parameters of crystalline material which comprises only a portion of a real sample out of polyethylene or most other polymers. This does not matter if the experimental method is sensitive only to the crystalline phase (X-ray, Far i.r.) but otherwise it causes confusion. Although the Grüneisen parameter of a semicrystalline specimen may still be a technically useful material constant, its molecular interpretation becomes impossible (the amorphous phase is not at all understood), the numerical values depend strongly on the sample preparation and clearly differ from the corresponding crystalline data (cf. *Table 3*). Therefore, we cannot compare them to results to be given here.

Semiempirical atomistic calculations

For the chemically most simple hydrocarbon chains containing only single bonds Hägele, Pechhold and coworkers[30,31] developed in 1970 a set of potential functions which have been used since then for the calculation of geometrical and energetic properties of several polymers[31–36,7] From the expression for the total energy comprising a rotational potential, a contribution from the bond angle deformation and the steric interaction we only need here the latter Buckingham term:

$$U_{\text{ster}} = \sum_{\substack{\text{H}\ldots\text{H} \\ \text{C}\ldots\text{H} \\ \text{C}\ldots\text{C}}} -Ar^{-6} + B\exp(-Cr)$$

the parameters of which are listed in *Table 1*. Vibrational frequencies were calculated according to the following procedure parts of which are similar to that described earlier[7].

Firstly, a chain together with its first shell of neighbouring chains is positioned in a lattice given by the X-ray data by Zugenmaier[37] and Ito[18]. The *a*- and *b*-axis values are listed in *Table 2*, for the *c*-axis Ito gives a strain of 0.13×10^{-3} kbar^{-1} which is thought to be negligible relative to the strains in the other two directions which are more than 50 times greater. (From the high pressure X-ray data available[14–18] we chose Ito's since they have been carefully determined in just the same pressure range as it is covered by our measurements presented here. Second shell calculations have been shown to be unnecessary[7]). Naturally, other lattices can also be fed into the computer, in particular a lattice strained only in one direction with the second axis stable. The setting angle is 42.7°.

Secondly, the central chain is moved as a stiff rod in the *a*- or in the *b*-direction in steps of 0.01 Å in both directions from the starting position and for each step the energy is

Table 1 Constants of the potential set

	H . . . H	C . . . H	C . . . C
A (kcal mol^{-1} Å^{-6})	33	128.5	500
B (kcal mol^{-1})	3000	14 000	53 000
C (Å^{-1})	3.74	3.67	3.60

Table 2 *a*- and *b*-axis of orthorhombic polyethylene as a function of pressure

p (kbar)	0	1	2	3	4	5	6	7
a (Å)	7.418	7.357	7.303	7.255	7.213	7.176	7.143	7.113
b (Å)	4.946	4.914	4.884	4.856	4.830	4.806	4.784	4.763

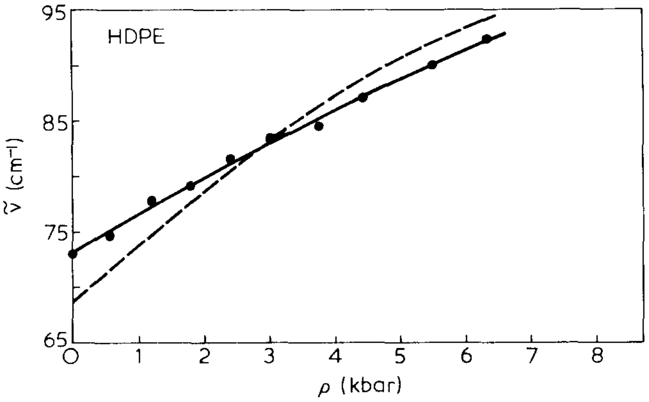

Figure 1 Experimental (●) and theoretical (— — —) pressure dependence of the frequency of the B_{1u}-lattice vibration at room temperature

calculated. In order to obtain it for one CH_2-group without border effects the computation has been done twice, once for a chain out of 14 CH_2 groups and then for another out of 16 CH_2 groups, half the difference being used in the further calculation.

Thirdly, assuming an amplitude of about 0.15 Å which is reasonable according to Iohara *et al.*[38] the energy values in this region were approximated by a parabola the second derivative of which gives the relevant force constant.

The calculations have been carried out with the setting angle variable in the range 39° to 51°. It turned out that for all pressure dependent lattice parameters the minimum frequency was exactly at the same setting angle of about 46° as in our earlier 0 K-0 bar-calculation (cf. *Figure 4* in ref. 7). Since then we chose a different angle in order to obtain the best agreement with experimental data we feel justified to use that very setting angle of 42.7° for all the lattices of the present calculations too, independent of pressure.

EXPERIMENTAL

An instrument was developed by modifying a Grubb-Parsons cube interferometer for use with a high pressure optical cell. The light from the lamp is made parallel and, after interference focussed on to a sample. This is a disc of about 4 mm thickness located between diamond type II-A windows in the centre of the optical cell. The pressure is generated in a hydraulic system and transmitted to the sample *via* silicone oil. In order to improve the signal to noise ratio by averaging, several data points are recorded for each mirror position.

The apparatus has been described in some detail elsewhere[6]. Samples were of linear polyethylene Lupolen 6011L from BASF and prepared by melting the polymer under vacuum at 190°C with subsequent slow cooling under a pressure of 500 bar in a piston type pressure vessel. The resulting density was 0.973 g/cm^3 which corresponds to a crystallinity of 83%.

RESULTS

Experiments

We have measured the B_{1u}-lattice vibration of polyethylene at room temperature and at several elevated temperatures covering a range of nearly 200 K. To the data points determined at room temperature a parabola can be fitted with the equation

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

Both points and the curve are shown in *Figure 1*. Similar curves determined at higher temperatures simply show a vertical shift towards lower frequencies, at least this is the first impression, and the length of the parallel shift is reasonable if compared with results on the temperature dependence[4] of the vibration as far as data are available determined at 0 bar. Details which will reveal an interesting phenomenon at elevated temperature and pressure shall be given elsewhere[39].

We may use the above equation for the pressure dependence of the B_{1u}-vibration frequency together with Ito's[18] formula for the relative volume change with pressure:

$$-\frac{\Delta V}{V_0} = 15.6\ 10^{-3}\ p\ \text{kbar}^{-1} - 0.84\ 10^{-3}\ p^2\ \text{kbar}^{-2} + 0.030\ 10^{-3}\ p^3\ \text{kbar}^{-3}$$

in order to evaluate the Grüneisen parameter

$$\gamma_V^{B_{1u}} = -\frac{\partial \ln \tilde{\nu}_{B_{1u}}}{\partial \ln V} = -\frac{\partial \ln \tilde{\nu}_{B_{1u}}}{\partial p} \frac{\partial p}{\partial \ln V}$$

For $p=0$ this yields a value of $\gamma_V^{B_{1u}} = 3.15$. An experimental uncertainty cannot be given because it is not known for the volume; for the frequency one may appraise the scattering of points in *Figure 1*.

This Grüneisen parameter as a function of pressure up to 7 kbar is shown in *Figure 2*. It increases considerably

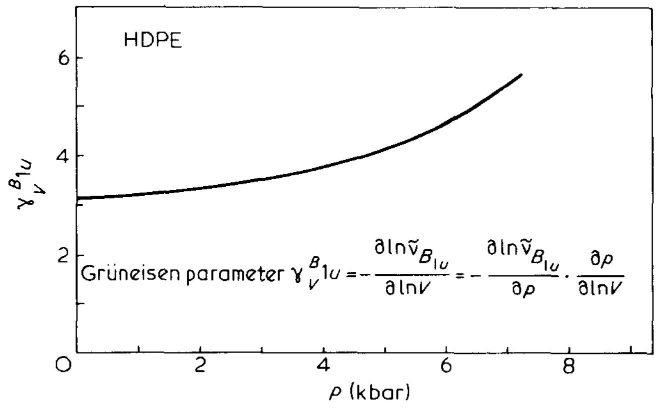

Figure 2 Grüneisen parameter as a function of pressure at room temperature

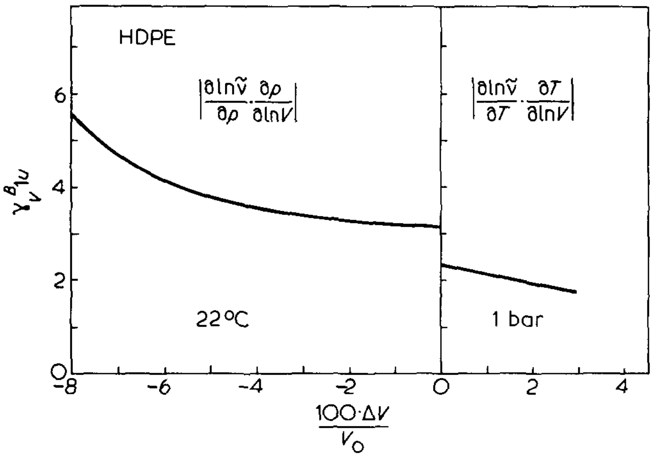

Figure 3 Grüneisen parameter as a function of relative volume change

and reaches almost 6. We should mention here that the calculation was carried out with $\partial \ln V = \partial V/V(p)$ and not with $\partial V/V_0$. Correspondingly, we used $\partial \ln\tilde{\nu} = \partial\tilde{\nu}/\tilde{\nu}(p)$. Naturally, *Figure 2* can be redrawn by replacing the pressure by the relative volume change. This has been done in the left part of *Figure 3* and will be used in the discussion.

Computations

Following the procedure described above, the frequency of the lattice vibration in the *b*-axis direction was calculated as a function of pressure. The result is given as the broken line in *Figure 1* and shows fair agreement with the experimental curve in spite of some deviations to be discussed later.

Furthermore the method has been invoked to evaluate the special (anisotropic) Grüneisen parameter of the B_{1u}-lattice vibration in the *a*-axis and in the *b*-axis direction. These two quantities are not directly accessible to the experiment in particular when no single crystals are available. Hence we calculated the frequency, firstly, as a function of b with constant a_0 and, secondly, as a function of a with constant b_0. The range wherein a and b were varied corresponds to compressions caused by a pressure of nearly 2 kbar (cf. *Table 2*). *Figure 4* shows the calculated frequencies. From the slope of the two straight lines we may calculate the two special (anisotropic) Grüneisen parameters:

$$\gamma_a^{B_{1u}} = -\frac{\partial \ln\tilde{\nu}}{\partial \varepsilon_a} = 6.1$$

$$\gamma_b^{B_{1u}} = -\frac{\partial \ln\tilde{\nu}}{\partial \varepsilon_b} = 2.2$$

There is no direct comparison of these values with results from our experiments, but they can be inserted in the following equation

$$\frac{\mathrm{d}\ln\tilde{\nu}}{\mathrm{d}p} = \frac{\partial \ln\tilde{\nu}}{\partial \varepsilon_a}\frac{\partial \varepsilon_a}{\partial p} + \frac{\partial \ln\tilde{\nu}}{\partial \varepsilon_b}\frac{\partial \varepsilon_b}{\partial p} + \frac{\partial \ln\tilde{\nu}}{\partial \varepsilon_c}\frac{\partial \varepsilon_c}{\partial p}\ .$$

From X-ray studies[14,17,18] we know that the *c*-axis is almost incompressible, so that the third term on the right side vanishes, and we also know $\partial\varepsilon_a/\partial p$ and $\partial\varepsilon_b/\partial p$, 8.77×10^{-3} kbar^{-1} and 6.72×10^{-3} kbar^{-1}, respectively. The right side thus gives 7.4×10^{-2} kbar^{-1} in agreement with the initial slope of the theoretical curve of *Figure 1* derived from the same model, whereas the left side can be evaluzted from our measurements as 4.9×10^{-2} kbar^{-1}. Taking into consideration that the above equation consists of slopes of experimental curves and quantities involving the third derivative of a potential function we are well satisfied with the approximate agreement.

We can summarize these last results by emphasizing that according to the theoretical model the frequency of B_{1u}-lattice vibration is much more sensitive to changes of the *a*-axis although the chains oscillate in *b*-axis direction. It is not clear to us whether this is a necessary consequence of the transition moment being in the *a*-axis direction or a feature peculiar to this vibration.

DISCUSSION

Pressure experiment at room temperature

The effect of pressure on the frequency of the B_{1u}-lattice vibration is relatively strong; the frequency shift between 0 and 7 kbar amounts to about 21 wavenumbers and exceeds the 12 wavenumbers considerably which can be achieved by varying the temperature between 0 and 400 K[4]. This is not a consequence of the corresponding relative volume changes; that of pressure variation (8%)[18] is even somewhat smaller than that of temperature variation (10%)[8,9]. It rather reflects the different mechanisms of thermal expansion and of compression by external pressure; three aspects of this difference shall be outlined:

Firstly, potentials can be regarded as harmonic for very small amplitudes of vibration, i.e. very low temperatures, so that the frequency shift below 100 K is small (as it has been verified for translations[4] and librations[40]). Secondly, polyethylene undergoes the glass transition near 240 K[4,41,42] so that, according to Frank *et al.*[4], the temperature dependence of the frequency is diminished below the glass transition temperature. Both effects are not present in the high pressure experiment. Thirdly, thermal expansion driven by the lattice vibrations with finite Grüneisen Parameter is extremely anisotropic[8] whereas the orthorhombic lattice of polyethylene is compressed, in the lateral direction, almost uniformly:

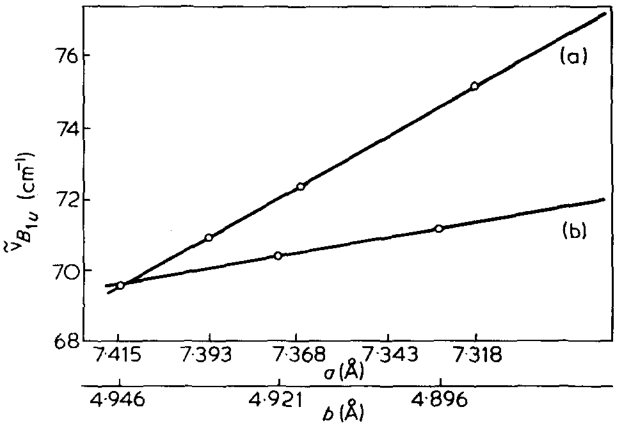

Figure 4 Frequency of the B_{1u}-lattice vibration as a function of lattice dimensions, calculated for compressions which would correspond up to about 2 kbar. In the upper curve (a) only the *a*-axis was varied, in the lower one (b) only the *b*-axis was varied

Table 3 Some experimental and theoretical Grüneisen parameters, determined near atmospheric pressure and room temperature

Static modulus				Ref.
γ	1.1–11.0	Various methods	see Wu *et al.* 1972	23
	6–7	Bulk volume measurements	Broadhurst and Mopsick 1970, 71	44, 45
	4.1	" " "	Warfield 1974	24
	3.4	X-ray study under pressure	Ito and Marui 1971	14
	3.64	" " " "	Sham *et al.* 1977	16
	3–3.5	" " " "	Nakafuku 1978	17
	3.0	" " " "	Ito 1979	18
Dynamic modulus				
γ	5.4	Sound velocity vs. pressure	Wada *et al.* 1969	26
	6.5	" " " "	Kijima *et al.* 1975, 76	46, 47
Spectroscopy				
γ_V^i	<0.1	High frequency bands as function of temperature or pressure	see Wu *et al.* 1972	23
	0.43	B_{1u} for materials of different density	Barker and Chen 1970	48
	3.8	Libration frequency vs. pressure	Wu 1975	19
	3.15	B_{1u}-frequency vs. pressure	This work	--
γ_a^{tr}	6.5	Transversal acoustic mode as function of temperature, $C_{33}H_{68}$	Strobl 1976	20
Theory				
γ_V^{tr}	3.16–3.5	Translational Grüneisen parameter	Curro 1973	49
$\gamma_a^{B_{1u}}$	6.1	Potential calculations	This work	–

The compressibilities (at $p=0$) in the a- and b-axis-direction are quite similar, 8.77×10^{-6} bar^{-1} and 6.72×10^{-6} bar^{-1} according to Ito[18]. For further illustration we have calculated the tensor of elastic coefficients (shear compliances omitted which is at room temperature in units of 10^{-5} bar^{-1}:

$$\begin{pmatrix} S_{aa} & S_{ab} & S_{ac} \\ S_{ab} & S_{bb} & S_{bc} \\ S_{ac} & S_{bc} & S_{cc} \end{pmatrix} = \begin{pmatrix} 3.2 & -2.1 & 0 \\ -2.1 & 2.6 & 0 \\ 0 & 0 & 0.03 \end{pmatrix}^{*}$$

If $\gamma_a > \gamma_b$, and the thermal expansion is dominated by change in a whereas the compression involves changes in both a and b, one might expect a frequency shift due to a 10% thermal expansion exceeding the shift due to an 8% compression, in disagreement with the observations. The first two effects mentioned above seem to prevail.

However, although thermal expansion differs from compression not only in sign, it can be used to check roughly the Grüneisen parameter evaluated from our experimental data. For this purpose the right part of *Figure 4* has been drawn using the results of Swan[8] and Frank *et al.*[4], which shows reasonable agreement in absolute value at 1 bar and ambient temperature as well as in trend. Further selected experimental and theoretical results are collected in *Table 3* and will be discussed now.

For appraisal of the various evaluation methods we recommend the reviews by Wu *et al.*[23] and Shen[25].

Certainly not comparable are the values obtained from the bulk modulus of semicrystalline samples[24,44,45] containing amorphous material. The contributions of the two phases cannot be distinguished; besides, in the amorphous state terms like lattice vibration have lost their meaning. Comparable**, however, and found to be in good agreement are the Grüneisen parameter from X-ray studies under high pressure[14,16–18]. There seems to be a systematic deviation when γ is determined from ultrasonic[26,46,47] techniques; perhaps, because semicrystalline material has been used. However, the authors[46] find γ of about 6 also for extended chain material from dilatometry and the temperature dependence reported differs in the sign of the slope from that of Frank[4] (*Figure 3*). By not varying the density of the crystal by temperature or pressure, but varying the density of polyethylene by using specimens of different crystallinity[48] elucidates, if anything, the influence of crystal size and perfection upon the vibration frequency, but not its volume dependence. To our knowledge the only lattice vibration investigated as a function of pressure at room temperature is an antiphase libration of adjacent chains about the chain axis and the Grüneisen parameter given by Wu[19] is very similar to ours. Finally, from the theoretical papers we should like to mention Curro's[49] who, using a Mie–Lennard-Jones 6–12 potential, derives from a thermodynamic cell model a Grüneisen parameter for translational motions somewhat below 3.5.

Computations

To calculate a vibrational frequency from a potential is

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* For its calculation we used the equations

$$-\frac{d\varepsilon_a}{dp} = S_{aa} + S_{ab} \quad , \quad -\frac{d\varepsilon_b}{dp} = S_{ab} + S_{bb}$$

and literature data for $\frac{d\varepsilon}{dp}$[18], S_{aa}[43], S_{bb}[43], S_{cc}[20] and the zeros[20]. The S_{ab} given is the average of the results from the two equations above, therefore $S_{aa}+S_{ab}$ and $S_{ab}+S_{bb}$ do not give the compressibilities quoted above.

** This holds under the assumption that the interchain vibrations all contribute the same amount to the average.

a severe test for the latter, since frequency is a function of the second derivative or of curvature. Additionally, assumptions have to be made which were in our calculations, firstly, an amplitude of about 0.15 Å, secondly a constant setting angle of 42.7° and thirdly the validity of Ito's volume data[18]. The problem arises, that for crystallography the samples were drawn and annealed whereas ours were crystallized under intermediate pressure and they were naturally of different material. Since minute discrepancies in volume are of consequence for the frequency this might be a source of error. To the problem of setting angle we have already outlined that from our calculations with variable setting angle we have no indication of any change. Furthermore, Wu and Jura[50] have experimental evidence from the i.r. intensities of split bending modes as a function of pressure that the setting angle is not changed with pressure. Alternatively, there is the result of Hikosaka *et al.*[15] suggesting a decrease of setting angle.

These authors have measured the *a*- and *b*-axes of polyethylene up to 45 kbar by the use of a diamond anvil cell which causes the data points to scatter considerably in the low pressure region (<10 kbar) where the pressure might be not uniform and its determination is difficult and as such, their initial compressibility is about a quarter less than that reported elsewhere[16–18]. Subsequently they have positioned short chains of 9 CH_2-groups into the lattices obtained, calculated a Williams IV potential[51] as a function of pressure (i.e. lattice dimensions) and its minimum with respect to the setting angle. Thus they found a decrease of the angle from 42.4° at 1 bar to 38.2° at 40 kbar. However, since we do not agree with their experimental data and consider a computation with 9 CH_2-groups insufficient, we have not though it necessary to use a pressure dependent setting angle in our calculations.

Thirdly, we should like to point out that it is not improbable that the amplitude of vibration is pressure dependent. An increase at low pressure would shift the calculated curve in *Figure 1* upwards, a decrease at high pressure would bring it down so that the deviation from the experimental curve would diminish. But since we had no indication on how strong the dependence was we had to use a constant amplitude as a first approximation.

It also has to be stated, that in our computations, interaction with other modes cannot be taken into account. Such interaction exists, it gives rise to thermal expansion (the data in *Table 2* are no equilibrium positions with respect to the intermolecular potential); still 'there is no contribution of the skeletal bending and torsional modes to the zone-centre modes[13]. Although of interest, the motion of molecules which are not stiff, would render computations too difficult at present.

In the literature we found only one experimentally determined special (anharmonic) Grüneisen parameter (see *Table 3*). Strobl[20] observed the temperature dependence of the Raman-active transversal acoustical modes and extrapolated γ_a^{tr} to about 6.5 which should be comparable to our $\gamma_a^{B_{1u}}$ of 6.1. Thus, from this different method our data receives additional strong support.

We can therefore draw the conclusion that the study of lattice vibrations at elevated pressure is useful in characterizing intermolecular interactions by Grüneisen parameters and to probe intermolecular potential functions.

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