

Lattice-Frequency Studies of Crystalline and Fold Structure in Polyethylene

M. I. BANK AND S. KRIMM

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

The assignment of the 71 cm^{-1} band in the infrared spectrum of polyethylene to the B_{1u} translational lattice vibration has been confirmed by dichroism studies on an a -axis oriented sample. This permits confident use of the Tasumi-Krimm calculations for the dependence of this frequency on unit-cell parameters. The results of these calculations have been applied to the analysis of the observed lattice frequency differences between odd and even n -paraffins, and it is shown that the frequency shifts are interpretable in terms of changes in unit cell parameters resulting from different methyl end-group packing. The variation of the lattice frequency with degree of branching observed in a series of low-density polyethylenes can be understood on the basis of incorporation of branches in the lattice. The dependence of the lattice frequency in high-density polyethylene on the physical state of the specimen can be correlated with different constraints imposed by the fold regions on the chain packing. These results indicate that the folds must be considered to be "tight" rather than "loose."

INTRODUCTION

The possibility that crystalline polyethylene could exhibit infrared-active translational lattice vibrations was first explicitly shown by a group-theoretical analysis of the spectrum.¹ The observation of a low-frequency ir band, at about 71 cm^{-1} , which was associated with the crystalline component of the polymer^{2,3} led to the suggestion³ that this band originated from one of the two allowed¹ translational lattice modes. This was further supported by the demonstration⁴ that this band was absent in n -paraffins containing only one chain per unit cell, and by the observation that the frequency of the comparable band in a deuteroparaffin was lowered by just the amount expected for a translational vibration.⁴ The assignment of this band to the B_{1u} lattice mode was strongly indicated by normal coordinate calculations of the vibrational spectrum of the crystal.^{5,6}

Since a lattice vibration in the crystal of polyethylene originates from the intermolecular forces between the two chains in the unit cell,⁷ and since these forces are determined by the separation and relative orientation of the chains, it becomes possible to use the lattice frequency as a probe of intermolecular interactions. We have studied the characteristics of this frequency in n -paraffins and in low-density and high-density polyethylenes, and we find that shifts in the position of this band reflect structural changes in the unit cell. Furthermore, the dependence of the frequency on sample preparation for a high-density polyethylene permits deductions concerning some characteristics of the fold structure in crystalline polyethylene.

¹ S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, *J. Chem. Phys.* **25**, 549 (1956).

² A. O. Frenzel and J. P. Butler, *J. Opt. Soc. Am.* **54**, 1059 (1964).

³ J. E. Bertie and E. Whalley, *J. Chem. Phys.* **41**, 575 (1964).

⁴ S. Krimm and M. I. Bank, *J. Chem. Phys.* **42**, 4059 (1965).

⁵ M. Tasumi and T. Shimanouchi, *J. Chem. Phys.* **43**, 1245 (1965).

⁶ M. Tasumi and S. Krimm, *J. Chem. Phys.* **46**, 755 (1967).

⁷ C. W. Bunn, *Trans. Faraday Soc.* **35**, 482 (1939).

ASSIGNMENT AND STRUCTURE DEPENDENCE OF THE 71 cm^{-1} BAND

In order to be able to use the 71 cm^{-1} band for structural studies, there must be complete certainty about its assignment. We have noted that deuteration studies are consistent with an assignment to a lattice translational mode,⁴ and that normal coordinate calculations predict this band to be the B_{1u} mode.^{5,6} We now present dichroism data which support this assignment.

The B_{1u} lattice mode corresponds to a translatory motion parallel to the b axis of the crystal with an oscillating dipole moment parallel to the a axis.¹ In an appropriately oriented sample, therefore, the 71 cm^{-1} band should show a -axis polarization. It has been shown⁸ that in machine-extruded polyethylene sheet the a axis is oriented parallel to the machine direction. Such orientation was verified for a sample of machine-extruded Marlex 6000 film by examination of the dichroism of the $720, 731\text{ cm}^{-1}$ CH_2 rocking mode doublet.⁸ The results are shown in Fig. 1(a), where it is seen that the 731 cm^{-1} component, which is known to correspond to an oscillating dipole moment parallel to the a axis,^{8,1} is polarized parallel to the machine direction.

The polarized spectrum of this Marlex 6000 film in the 70 cm^{-1} region is shown in Fig. 1(b). (The spectrum was obtained using 84 layers of the film with Nujol placed between the layers to reduce scattering.) It will be seen that the 71 cm^{-1} band is polarized parallel to the machine direction. This shows that it has a -axis dichroism, and makes its assignment to the B_{1u} lattice mode compelling. The recent observation⁹ in a 2°K spectrum of polyethylene of an additional weak band at about 110 cm^{-1} , almost exactly the value predicted for the B_{2u} lattice mode,^{5,6} should give us complete confidence in the assignment

⁸ S. Krimm, *J. Chem. Phys.* **22**, 567 (1954).

⁹ G. D. Dean and D. H. Martin, *Chem. Phys. Letters* **1**, 415 (1967).

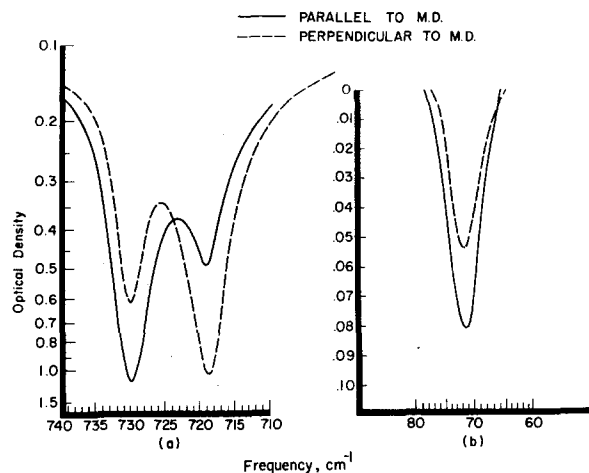


FIG. 1. Polarized ir spectra of machine-extruded Marlex 6000 polyethylene film (a) in the 700 cm^{-1} region and (b) in the 70 cm^{-1} region. —: electric vector parallel to the machine direction; - - -: electric vector perpendicular to the machine direction.

of the 71 cm^{-1} band to the B_{1u} lattice vibration (hereafter referred to as ν_{1l}).

The forces responsible for this lattice vibration arise from interchain interactions, presumably mainly atom-atom interactions between H atoms on neighboring chains.^{5,6} In Fig. 2 we show the four important (i.e., shortest) $\text{H}\cdots\text{H}$ distances (q_1 , q_2 , q_3 , and q_4), and the remaining interactions which result from these by operation of the symmetry elements of the unit cell. It will be seen that any given chain interacts directly with its six nearest neighbors. The total energy of interaction is a function of the values of the distances q_1 through q_4 , and it is clear that these will depend on the unit cell dimensions and the setting angle θ (see Fig. 2).

The dependence of ν_{1l} on the above lattice parameters has been determined in part.⁶ For example, ν_{1l} was calculated for unit cell dimensions at room temperature ($a=7.414\text{ \AA}$, $b=4.942\text{ \AA}^{11}$) and at liquid-nitrogen temperature ($a=7.155\text{ \AA}$, $b=4.899\text{ \AA}^{11}$) for $\theta=48^\circ$. The calculated frequencies, viz., 71.1 cm^{-1} and 80.6 cm^{-1} , respectively, are in good agreement with those found experimentally.³ For each of these unit cell dimensions, ν_{1l} was calculated as a function of θ for several potential functions. Although the variation depended somewhat on the potential function used, it was relatively uniform and equivalent to about $\Delta\nu_{1l}/\Delta\theta = -0.8\text{ cm}^{-1}/\text{deg}$. Such calculations also indicated that for $41.5^\circ < \theta < 48^\circ$ there was an approximately constant change of ν_{1l} with cross-sectional area ($a\cdot b$) equal to $\Delta\nu_{1l}/\Delta(a\cdot b) = 2.7_6\text{ cm}^{-1}/\%$ decrease in $a\cdot b$. While these figures are to some extent dependent on the assumed potential function, they nevertheless should provide reasonable estimates of how ν_{1l} will be affected by changes in the structural parameters of the unit cell.

EXPERIMENTAL

1. Sample Preparation

A series of normal paraffins ($\text{C}_{27}\text{H}_{56}$, $\text{C}_{29}\text{H}_{60}$, $\text{C}_{30}\text{H}_{62}$, and $\text{C}_{36}\text{H}_{74}$) were studied. These were crystallized by cooling to room temperature a solution of the paraffin in benzene and then evaporating the solvent. The resulting crystals were then pressed in a die (of $\frac{7}{8}$ in. \times $\frac{3}{8}$ in. cross section) to give a specimen of the required thickness.

The polyethylenes which were used were commercial polymers; their branching ratios were taken as given by the manufacturer. Samples were crystallized from the melt by heating the polymer in the above-mentioned die to $T > 140^\circ\text{C}$, and allowing it to cool (at about $2^\circ\text{--}3^\circ\text{C}/\text{min}$), while applying a small force (about 500 lb). Densities of these samples were determined by the flotation method in methanol.

Two samples of solution-grown crystals were prepared. For the first, designated SC-10, single crystals were obtained by crystallizing Marlex 6009 from a 0.1% solution in xylene at 79°C . After 24 h the solution was filtered (through a microfine fritted disk filter) to give a mat of single crystals. In order to obtain enough material (about 450 mg), the process was repeated ten times. The individual samples were dried in an oven at 55°C , and the resulting mats were compressed in a die under about 5000 lb force to a sample of dimensions $\frac{7}{8}$ in. \times $\frac{3}{8}$ in. \times 0.061 in. The

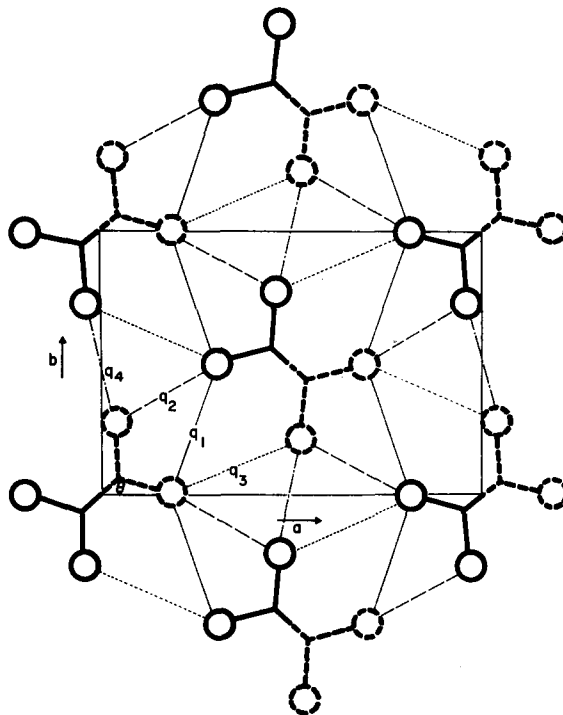


FIG. 2. Cross section of the unit cell of polyethylene, showing the important (i.e., short) $\text{H}\cdots\text{H}$ contacts (q_1 , q_2 , q_3 , and q_4) as well as the equivalent interactions generated by symmetry.

second sample, designated CF-1, was prepared by casting films of Marlex 6009 from a 0.5% solution in xylene. The solvent was evaporated in an oven at 50°C over a period of at least 12 h. The films were removed from the petrie dishes by soaking in CS₂, dried, and then pressed in the above die to a sample of thickness 0.069 in.

2. Spectroscopy

Spectra were obtained on a Perkin-Elmer model 301 Spectrophotometer calibrated with water-vapor rotation lines. The absolute accuracy in determining the positions of well-defined bands is ± 0.250 cm⁻¹; the relative accuracy for different samples is ± 0.125 cm⁻¹. The temperature at the sample is normally 30°C.

Low-temperature spectra were obtained by conduction-cooling of samples held in contact with a liquid-nitrogen cooled copper sample holder. Thermocouples were placed in contact with the sample to measure the temperatures of the front and rear surfaces (the latter was in more optimum contact with the copper block). Temperature gradients between the surfaces were found in all cases, due to the thickness and low thermal conductivity of the sample. The lattice frequency was sensitive to temperature, but it was found in general that if the front surface temperature was lower than about -120°C, there was little or no measurable change of lattice frequency with diminishing temperature. Most samples were run as close as possible to this condition.

3. X-Ray Diffraction

The *a*-axis and *b*-axis unit-cell dimensions were determined using a Norelco diffractometer with scintillation counter detector. Calibration was done with a silicon standard. The (200) and (110) polyethylene reflections were scanned at a rate of $\frac{1}{4}^\circ$ in 2θ /min. The relative accuracy (which is mainly a function of reproducibility in sample positioning) is estimated to be $\pm 0.03^\circ$ for the (200) reflection and $\pm 0.02^\circ$

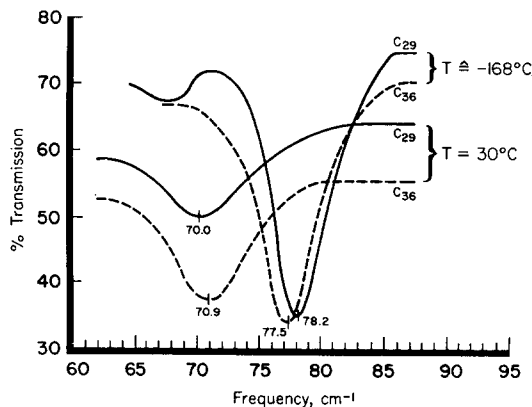


Fig. 3. B_{1u} lattice frequency of n -C₂₉H₆₀ (—) and n -C₃₆H₇₄ (---), at room temperature and at about -168°C.

TABLE I. B_{1u} lattice frequency in n -paraffins.

Paraffin	Structure	ν_{11} (cm ⁻¹)	
		$T = 30^\circ\text{C}$	$T \cong -168^\circ\text{C}$
C ₂₇ H ₅₆	Orthorhombic ^a	70.0	78.1
C ₂₉ H ₆₀	Orthorhombic ^a	70.0	78.2 ₅
C ₃₀ H ₆₂	Monoclinic ^b	70.9	77.9
C ₃₆ H ₇₄	Monoclinic ^b	70.9	77.5

^a $a = 7.47_8 \pm 0.01$ Å, $b = 4.97_0 \pm 0.01$ Å, $\theta = 44^\circ$.

^b $a = 7.42 \pm 0.01$ Å, $b = 4.94_5 \pm 0.01$ Å, $\theta = 48.6^\circ$ (for orthorhombic subcell).

for the (110) reflection, which corresponds to ± 0.009 Å in the *a*-axis dimension and ± 0.015 Å in the *b*-axis dimension. Our values for these spacings are commensurate with those obtained by other authors.^{10,11}

RESULTS AND DISCUSSION

1. *n*-Paraffins

The ν_{11} lattice-vibration frequency was studied in a series of n -paraffins in order to check the theoretical predictions on a relatively well-defined model system. Spectra were obtained for C₂₇H₅₆, C₂₉H₆₀, C₃₀H₆₂, and C₃₆H₇₄ at room temperature and at low temperature. The spectra of the odd paraffins were similar, as was the case for the even paraffins, but the two groups differed from each other. Spectra for C₂₉H₆₀ and C₃₆H₇₄ are shown in Fig. 3, and the frequencies for all of the samples are given in Table I.

It will be seen that in the room-temperature spectra ν_{11} is observed at 70.0 cm⁻¹ for the odd paraffins and at 70.9 cm⁻¹ for the even paraffins. Crystal-structure determinations have shown that at room temperature the odd paraffins are orthorhombic¹² with unit cell parameters: $a = 7.47_8 \pm 0.01$ Å, $b = 4.97_0 \pm 0.01$ Å, $\theta = 44^\circ$,¹³ while the even paraffins are monoclinic¹⁴ with orthorhombic subcell parameters: $a = 7.42 \pm 0.01$ Å, $b = 4.94_5 \pm 0.01$ Å, $\theta = 48.6^\circ$ (the latter dimensions are for C₃₆H₇₄; it is assumed that they apply as well for C₃₀H₆₂). It is of interest to see if the shift in frequency can be accounted for by the calculated variation with structural parameters referred to earlier. For the observed decrease in unit cell area from odd to even paraffins, viz., $1.27 \pm 0.66\%$, an increase of $(1.27 \pm 0.66) \times 2.7_6 = 3.5 \pm 1.8$ cm⁻¹ in ν_{11} is predicted. For the observed increase in setting angle from odd to even paraffins, viz., 4.6° , a decrease of $4.6 \times 0.8 = 3.7$ cm⁻¹ in ν_{11} is predicted (Unfortunately, no error is given in the determination of θ in the crystal-structure

¹⁰ E. A. Cole and D. R. Holmes, J. Polymer Sci. **46**, 245 (1960).

¹¹ P. R. Swan, J. Polymer Sci. **56**, 403 (1962).

¹² A. E. Smith, J. Chem. Phys. **21**, 2229 (1953).

¹³ While Smith¹² gives $\theta = 42^\circ$, L. Salem, J. Chem. Phys. **37**, 2100 (1962) quotes Smith (private communication) as giving $\theta = 44^\circ$.

¹⁴ H. M. Shearer and V. Vand Acta Cryst. **9**, 379 (1965).

TABLE II. B_{1u} lattice frequency in various polyethylenes.

Sample	t^a	CH ₂ /1000 C	ρ	a (Å)	b (Å)	ν_{1l} (cm ⁻¹)	
						$T=30^\circ\text{C}$	$T\cong-170^\circ\text{C}$
Fortiflex A60-500	0.0996	0	0.965	7.424	4.947	72.3	78.1
Marlex 6009	0.117	0	0.962	7.414	4.947	72.3	78.1
Alathon 7050	0.129	0	0.960	7.419	4.940	72.3	78.0
Marlex 5003 ^b	0.128	2.1	0.953	7.445	4.959	72.0	77.8
Fortiflex B45-600	0.166	...	0.949	7.454	4.958	71.7	77.5
Alathon 4995	0.177	24.4	0.934	7.492	4.954	71.3	77.0
Alathon 34	0.288	15.7	0.930	7.498	4.982	71.5	77.1
Marlex 2130	0.258	...	0.922	7.504	4.984	71.0	77.3
Alathon 10	0.360	24.6	0.922	7.501	4.978	71.0	77.1
Alathon 18	0.365	32	0.916	7.506	4.977	70.8	76.9
Alathon 17	0.254	22.7	0.908	7.493	4.974	70.6	77.0
Alathon 1414	0.310	37.9	0.894	7.529	4.993	70.4	76.9

^a Thickness of room-temperature specimen, in inches.^b Ethylene-butene-1 copolymer (0.9% butene-1).

analyses.) Thus, a decrease of 0.2 ± 1.8 cm⁻¹ is predicted between odd and even paraffins, compared to an observed increase of 0.9 cm⁻¹. The observed shift, however, is well within the limits of the predicted range. More refined structure determinations would be required in order to provide a more sensitive test of the theory. It is apparent, therefore, that the theoretical calculations⁶ provide a reasonably satisfactory basis for relating changes in ν_{1l} to changes in a , b , and θ .

The increase in ν_{1l} with decreasing temperature (see Table I) is expected,⁶ since the a and b dimensions of the unit cell decrease as a result of contraction.^{10,11} The frequency shift, however, is different for the odd and even paraffins, being about 8.2 cm⁻¹ (11.7%) for the former and about 6.8 cm⁻¹ (9.6%) for the latter. Detailed structure determinations are not available for paraffins at low temperatures. The unit cell dimensions of C₃₆H₇₄ at -150°C have, however, been reported,¹⁰ being $a=7.19_5$ Å, $b=4.86_7$ Å. This represents a 4.55% decrease in cross-sectional area as compared to the room-temperature structure, which would give a 12.6 cm⁻¹ increase in ν_{1l} . The observed increase of about 6.5 cm⁻¹ (assuming no significant structural change between -150° and -168°C) is much less than this, which would imply a compensating increase in θ at low temperatures (an increase of about 7.5° would be required to give agreement with the observed $\Delta\nu_{1l}$). No detailed information is available on this point, although preliminary structure studies on polyethylene at -100°C ¹⁵ definitely show that θ increases with decreasing temperature. It is therefore not possible in this case to provide a check of the theory, although the experimental observations are in good qualitative agreement with the predictions.

It remains to comment on the difference in ν_{1l} between the odd and even paraffins at room tempera-

ture, and the difference in $\Delta\nu_{1l}$ as the temperature is lowered. It is clear that the difference in ν_{1l} , which is a consequence of the differences in a , b , and θ , is directly attributable to the constraints on the structure imposed by different end-group packing arrangements. The orthorhombic structure has its chains perpendicular to the plane formed by the end methyl groups whereas in the monoclinic structure the chains are tilted with respect to this plane.^{12,14,16} This imposes different restrictions on the end-group packing,^{17,18} and hence on the unit cell parameters. It is also likely that the contraction behavior with decreasing temperature will be different for the two kinds of end-group arrangements, thus explaining the difference in $\Delta\nu_{1l}$ under these conditions. [A more detailed study of the model structures is required to show why $\Delta\nu_{1l}(\text{odd}) > \Delta\nu_{1l}(\text{even})$.] It should be noted that these results show that the end-group constraints are propagated through the crystal, i.e., the chain retains its planar zig-zag structure and does not change over into a common structure within the lattice. This was of course apparent from the structure determinations on the n -paraffins^{12,14,16}; it has also been indicated to be true from spectroscopic arguments for polyethylene.¹⁹

2. Polyethylenes

A. Dependence on Branching

The ν_{1l} lattice vibration frequency of polyethylene would be expected to depend upon unit cell parameters in a manner similar to that found for the n -paraffins. Such parameters have been found to be related to the degree of perfection of the chain (which is correlated with the degree of branching) and to the

¹⁶ P. W. Teare, *Acta Cryst.* **12**, 294 (1959).¹⁷ T. Malkin, *Trans. Faraday Soc.* **29**, 977 (1933).¹⁸ M. G. Broadhurst, *J. Res. Natl. Bur. Std.* **66A**, 241 (1962).¹⁹ S. Krimm, M. Tasumi, and C. G. Opaskar, *Polymer Letters* **5**, 105 (1967).¹⁵ N. Kasai and M. Kakudo, Preprint P491, IUPAC *Symposium on Macromolecular Chemistry* (Prague, 1965).

physical state of the polymer. In this section, we consider the effects of branching, leaving a consideration of the influence of physical state for the next section.

A series of different polyethylenes were examined as samples crystallized from the melt. Their densities were measured, x-ray diffraction patterns obtained, and spectra scanned at room temperature and at about -170°C . The results are collected in Table II, together with information on the degree of branching (presented as number of CH_3 groups per 1000 carbon atoms, where available from the manufacturer). In Fig. 4 the spectra of four of these samples are shown, both at room temperature and at low temperature. (For the low-temperature spectra the specimens were thinner than for the room-temperature spectra in order to guarantee that the temperature of the front surface was lower than -120°C . The increase in intensity of ν_{11} with decreasing temperature³ made this procedure feasible.)

Several features of the data are of interest. First, it will be seen that samples of higher crystallinity (i.e., lower branching) have more intense ν_{11} bands than samples of lower crystallinity (i.e., Table II shows that thinner specimens are required for the more highly crystalline polymer in order to obtain comparable band intensities). This is undoubtedly due primarily to the crystalline origin of the ν_{11} mode, as previously noted. Second, with decreasing crystallinity the ν_{11} frequency is lowered. This is accompanied by decreasing densities and increasing unit cell dimensions. In fact, ν_{11} seems to be correlated almost linearly with density and with the a -axis dimension, as can be seen in Fig. 5. Third, ν_{11} for any given polymer increases with decreasing temperature. The absolute and relative increases are somewhat larger

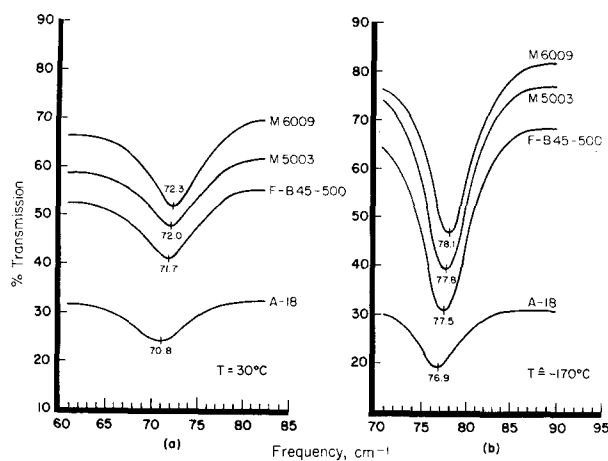


FIG. 4. B_{1u} lattice frequency of various polyethylenes (a) at room temperature and (b) at about -170°C (see Table II for detailed information on samples). In (a) the % transmission scale applies to all curves. In (b), two curves have been shifted as follows: M6009 by $+14\%T$, A18 by $-30\%T$.

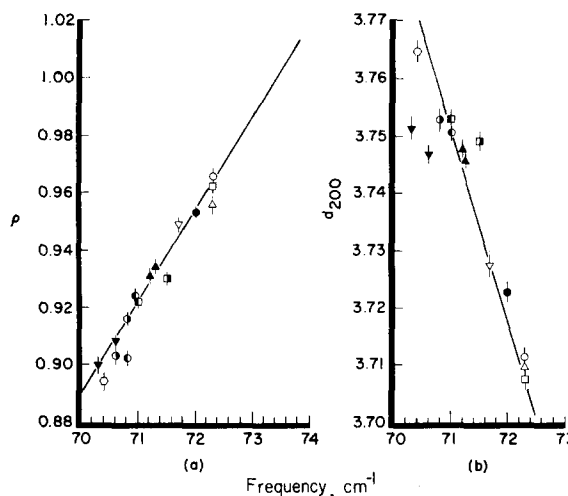


FIG. 5. Variation of B_{1u} lattice frequency of various polyethylenes (a) with density and (b) with d_{200} x-ray spacing. (See Table II for details on samples. For some polymers different density lattice-frequency values were found on two different samples; these are shown by the same symbol.)

for the less crystalline polymers, although their ν_{11} frequency never reaches as high a value as that for the most crystalline polymers.

These features of the behavior of the ν_{11} lattice vibration are consistent with the incorporation of branches into the lattice as defects. This results in an expansion of the lattice and an increase in the unit cell dimensions, a characteristic already observed in x-ray diffraction studies.^{10,20-24} It has been suggested²⁴ that, while for methyl branches the expansion is essentially independent of crystallization conditions, for propyl branches the unit cell dimensions are markedly dependent on the conditions under which crystallization occurs. The presence of some triclinic polymorph has also been inferred²⁴ for crystallization taking place below 90°C for the more highly branched polymers.

As we observed earlier, the decrease in intensity of the ν_{11} band with decreasing crystallinity is primarily related to the crystalline origin of this mode. It should be emphasized that this vibration is associated, however, only with the orthorhombic unit cell, being absent for the triclinic cell.⁴ Therefore, if by analogy with the above suggestion,²⁴ an increasing amount of the triclinic polymorph is formed in the case of the more highly branched polymer, the decrease in intensity of the ν_{11} band will not truly reflect the percentage decrease in total crystallinity. The data of Fig. 4 and Table II, however, do not suggest

²⁰ E. R. Walter and F. P. Reding, *J. Polymer Sci.* **21**, 561 (1956).

²¹ R. M. Eichorn, *J. Polymer Sci.* **31**, 197 (1958).

²² C. Sella, *Compt. Rend.* **248**, 2348 (1959).

²³ P. R. Swan, *J. Polymer Sci.* **56**, 409 (1962).

²⁴ C. H. Baker and L. Mandelkern, *Polymer* **7**, 71 (1966).

the presence of a significant amount of triclinic structure in, for example, Alathon 18, since its crystallinity (assuming a constant extinction coefficient) is about 37% of that of the Marlex 6009, a figure which is roughly in agreement with that obtained by other methods for a polymer with this degree of branching.²⁵ The good correlation of ν_{1l} with a -axis spacing (Fig. 5) also indicates the absence of any marked contribution of the triclinic polymorph to the measured spacings,²⁴ at least for samples no less crystalline than Alathon 18.

The decrease in the ν_{1l} frequency with decreasing crystallinity points to the incorporation of the branches into the lattice, with a consequent general expansion of unit cell dimensions. The exact value of ν_{1l} of course depends upon θ as well as on a and b , and if we accept the figures given earlier, this can be calculated. For example, the percentage decrease in cross-sectional area between Alathon 1414 and Marlex 6009 is 2.43%, which should correspond to a frequency increase of $2.43 \times 2.76 = 6.7 \text{ cm}^{-1}$. Since the frequency increases by only $72.3 - 70.4 = 1.9 \text{ cm}^{-1}$, the compensatory change in θ must be a decrease of $4.8/0.8 = 6^\circ$. The actual value of θ is of course unknown for the low-density polymers, but the above change would at least be qualitatively consistent with the observed decrease in θ with increase in a -axis dimension.¹⁵ (The internal consistency of the above type of calculation can be checked as follows, viz., by calculating θ for the high-density polymer in two essentially independent ways. For example, since the unit cell of the even n -paraffins has essentially the same cross-sectional area as that of the high-density polyethylene, the increase in ν_{1l} of $72.3 - 70.9 = 1.4 \text{ cm}^{-1}$ should be attributable to a decrease in θ of $1.4/0.8 = 1.8^\circ$. Therefore, if we assume that $\theta = 48.6^\circ$ for the even n -paraffin, its value for the high-density polyethylene should be 46.8° . On the other hand, the decrease in cross-sectional area between the odd n -paraffins and high-density polyethylene is 1.35%, implying an expected increase in ν_{1l} of $1.35 \times 2.76 = 3.7 \text{ cm}^{-1}$ over the paraffin frequency. The smaller increase of $73.7 - 72.3 = 1.4 \text{ cm}^{-1}$ would then be attributable to an increase of $1.4/0.8 = 1.8^\circ$ in θ over the value of 44° in the paraffin, i.e., to an expected value of 45.8° in the polymer. The two predicted values (46.8° and 45.8°) are probably as close to equality as can be expected from such calculations in view of the present state of the theory and the uncertainty in θ for the n -paraffin structures. Incidentally, these calculations suggest that a value somewhat lower than the 48° used in the normal coordinate analysis⁶ might have to be considered.)

The increase in ν_{1l} with decreasing temperature for all of the polymers is, of course, to be expected as a result of the thermal contraction of the unit cell. The somewhat more expanded lattices of the less

crystalline polymers can probably contract relatively more with temperature than those of the polymers with higher crystallinity, thus explaining the slightly larger $\Delta\nu_{1l}$ of the former. The branches, however, impose restrictions which prevent ν_{1l} from attaining the value reached by the high-density polymers. This is further evidence supporting the idea that the branches are incorporated in the lattice.

Finally, we should note that we have obtained preliminary evidence which suggests that ν_{1l} for a low-density polymer may depend upon crystallization conditions. For example, a sample of Alathon 17 was prepared whose density was found to be 0.900 (with $a = 7.503 \text{ \AA}$ and $b = 4.964 \text{ \AA}$) and whose lattice frequency was 70.3 cm^{-1} . An Alathon 18 of density 0.903 had $\nu_{1l} = 70.6 \text{ cm}^{-1}$, and an Alathon 10 of density 0.902 had $\nu_{1l} = 70.8 \text{ cm}^{-1}$. In all of these cases the density is lower than the maximum density obtained (cf. Table II), and ν_{1l} is also found to be lower than the maximum observed value. Although a systematic study as a function of crystallization conditions remains to be done, the indications at present suggest that when samples of a given polymer are prepared which have a lower than achievable density, then ν_{1l} will be correspondingly lower. This could result from a greater inclusion of branches in the lattice of the lower density sample, with an attendant expansion of the lattice and/or change in θ , analogous to the similar effect noted with respect to x-ray reflections.²⁴

B. Dependence on Physical State

While a dependence ν_{1l} on the degree of perfection of the chain might be anticipated, a variation of ν_{1l} with physical state of the specimen is somewhat more surprising. That such a variation exists is shown by the data in Table III and Fig. 6. Lattice frequencies are given for a Marlex 6009 polymer prepared as a cast film (CF-1), in the form of single crystals (SC-10), and as a melt-crystallized sample. For comparison ν_{1l} of a high-pressure melt-crystallized linear polyethylene (XC) is given.

It will be seen from Table III that ν_{1l} is higher for the melt-crystallized sample (MC) than for the solution-grown specimens (CF-1 and SC-10), and is highest for the high-pressure melt-crystallized polymer. This sequence is maintained at low temperature, although increased frequency shifts for the melt-crystallized samples enhance the difference between their frequencies and those of the solution-grown specimens. Using the MC sample as a comparison, calculations of the previous type show that θ has decreased by 2.6° for CF-1 and by 2.0° for SC-10 from its value in the MC specimen. (Within the errors of this type of calculation, these values should probably be considered equivalent.) The changes in ν_{1l} with physical state are thus clearly associated with changes in a , b , and θ , with an indication that

²⁵ F. P. Reding and C. M. Lovell, *J. Polymer Sci.* **21**, 157 (1956).

TABLE III. B_{1u} lattice frequency of linear polyethylene. ^a

Physical state	Lattice dimensions (Å)		ν_{11} (cm ⁻¹)	
	<i>a</i>	<i>b</i>	<i>T</i> = 30°C	<i>T</i> ≈ -170°C
Cast film (CF-1)	7.445	4.975	71.7	76.4
Single crystal (SC-10)	7.435	4.970	71.8	76.6
Melt crystallized (MC)	7.414	4.947	72.3	78.1
(High P crystallized ^b -XC)	72.7	78.4

^a Marlex 6009.^b Marlex 50.

there is a relatively larger change in these parameters between solution-grown and melt-crystallized specimens than between the solution-grown samples.

The dependence of ν_{11} on physical state is undoubtedly related to differences in fold structure between specimens prepared in different ways. One possibility that needs to be considered is that ν_{11} can vary with the length of planar zigzag chain. It is known that this length is a function of crystallization conditions through the dependence of fold period on crystallization temperature. Thus, we can expect²⁶ that the planar zigzag length would be about 90 Å for CF-1, about 120 Å for SC-10, and of the order of several hundred Å for MC. The XC sample is believed to contain mostly extended chains,^{27,28} thus implying planar zig-zag lengths of upwards of several thousand angstroms. It might be thought that unit cells near the surface of folded chain crystals could

be constrained by the folds so as to have larger cell dimensions, but that these constraints would lessen in the interior of the crystal thus permitting closer approach of the chains. This would predict that the larger the lamellar thickness the higher should be ν_{11} , which would nominally be in agreement with the data in Table III. We do not believe, however, that this explanation is compatible with the observations. The effect of such a continuum of structures would at the very least be to give a broader ν_{11} band for the CF-1 sample, where the heterogeneity of structure would be most pronounced.¹⁹ As can be seen from Fig. 6, there is no significant difference in half-widths of the bands, particularly at low temperature where the effect would be expected to be enhanced.

We believe that another mechanism is involved in causing ν_{11} to vary with physical state, viz., constraints imposed on the chains by different fold structures. On the basis of theoretical¹⁹ and experimental³⁰ studies of mixed crystals of polyethylene and perdeuteropolyethylene, it has been possible to show that in solution-grown crystals the chain folds occur (predominantly with adjacent reentry) along the (110) crystallographic planes, whereas in melt-crystallized crystals the folds are predominantly parallel to the *b* axis. Since the high-pressure crystallized polymer contains no folds, we have a situation in which three different classes of constraints can exist on the planar zigzag chain traversing the crystal. (We assume, by analogy with the *n*-paraffin structures, that the planar zigzag character of the carbon chain is maintained no matter what the constraints on the chain ends.)

In the extended chain polymer there are essentially no constraints on the chains. They are therefore able to take up the closest possible "approach," leading to the highest value of ν_{11} . They are also least constrained in contracting with decreasing temperature, thus exhibiting the highest low-temperature value of ν_{11} .

In the normal melt-crystallized polymer folding parallel to the *b* axis predominates. Although this may not impose major constraints along the *a*-axis direction, it could constrain the separation and/or setting angle, θ , of neighboring chains along the *b* axis. (This, of course, could then affect the *a*-axis

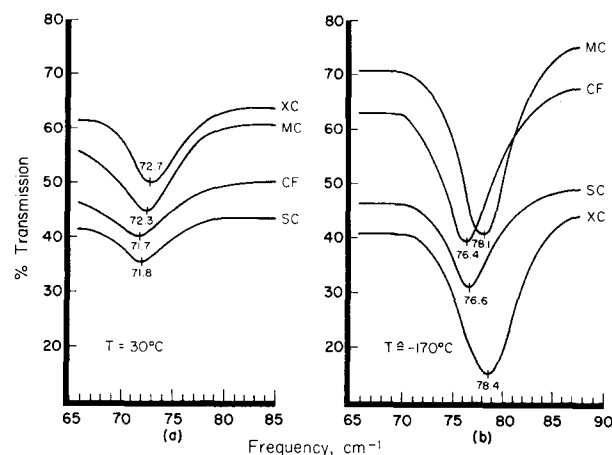


FIG. 6. B_{1u} lattice frequency of Marlex 6009 as a function of physical state (a) at room temperature and (b) at about -170°C. SC = single crystals, CF = cast film, MC = melt-crystallized sample, XC = extended chain (i.e., high-pressure crystallized) sample (Marlex 50 in this case). See text for further details on sample preparation. In (a) the curves have been shifted as follows: XC by +20%*T*, CF by -7%*T*, SC by -3%*T*. In (b) the curves have been shifted as follows: MC by +8%*T*, XC by -7%*T*.

²⁶ P. H. Geil, *Polymer Single Crystals* (Interscience Publishers, Inc., New York, 1963).

²⁷ B. Wunderlich and T. Arakawa, *J. Polymer Sci.* **A2**, 3697 (1964).

²⁸ P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polymer Sci.* **A2**, 3707 (1964).

²⁹ M. Tasumi and S. Krimm, *J. Polymer Sci.* **A26**, 995 (1968).

³⁰ M. I. Bank and S. Krimm (to be published).

dimension.) Alternatively, the packing of the folds themselves on the surfaces of the crystals may provide the dominant constraint. In any case, it is clear experimentally that the chains cannot adopt the close approach configuration which was feasible in the extended chain crystals. This is additionally apparent from the low-temperature behavior, in which $\nu_{11}(\text{MC}) < \nu_{11}(\text{XC})$: the constraints prevent the contraction from being as "efficient" as was possible in the extended chain case. (This is supported by unit cell dimensions of $\text{C}_{36}\text{H}_{74}$ and polymethylene obtained at -150°C ¹⁰: although the a -axis length is essentially the same, the b -axis length of $\text{C}_{36}\text{H}_{74}$ is smaller than that of polymethylene. This indicates the presence of a relative constraint on the contraction of the b axis as compared with that of the a axis.)

In the solution-crystallized polymer folding parallel to (110) predominates. Since the fold distance (i.e., the distance in the a - b plane from one chain to the next) in this case is different from that of the b -axis fold, there is no necessity that the fold geometry should be the same. As a result, either because of constraints on the fold distance or on θ , or because of differences in packing of the folds, a different set of unit cell parameters could result. The fold distance for a (110) fold (viz., 4.14 Å) is smaller than that for a b -axis fold (viz., 4.95 Å), and it is possible that the constraints on the main chains in making the former fold are more severe than in making the latter, thus resulting in $\nu_{11}(\text{CF-1, SC-10}) < \nu_{11}(\text{MC})$. It is, in any case, easy to understand why $\Delta\nu_{11}(\text{CF-1, SC-10}) < \Delta\nu_{11}(\text{MC})$: since the dominant contraction with temperature is that of the a axis,^{10,11} a fold [such as (110)] with an a -axis component is more likely to interfere with a shortening of the a axis than is a fold (such as the b -axis fold) which has no component along the a axis.

It appears, therefore, that the characteristic values of the ν_{11} lattice frequency can be interpreted in terms of constraints on the lattice structure: in the case of the n -paraffins the constraints arise from methyl end-group packing; in the case of low-density polyethylenes, the constraints originate from the incorporation of branches in the lattice; and in the case of the high-density polyethylenes the variations in ν_{11} with physical state arise from varying constraints associated with the different fold structures obtained with different conditions of crystallization.

FOLD STRUCTURE

The above results have definite implications with respect to the structure of the fold regions. The studies on mixed crystals³⁰ established the predominance of

adjacent reentry in well-defined crystallographic planes, thereby rendering unlikely any significant "switchboard" model³¹ component. The lattice-frequency results support the latter point, and suggest that the folds are "tight" rather than "loose."

If the "switchboard" model were to prevail, then in either solution-grown or melt-crystallized crystals there would be no necessary correlation between the orientation of a chain and that of its neighbors. This would imply: (a) no constraints on the main chains (if the connections were "loose")—in which case ν_{11} should equal that for the extended chain crystals (which is not true), or (b) a possible variation in θ (if the connections were "tight" and made in a random manner)—in which case the half-width of the ν_{11} band should be significantly smaller for the supposedly more uniform extended chain crystals (which is also not true). A "switchboard" model therefore seems to be substantially eliminated.

On the other hand, the data support the presence of "tight" folds. The fact that ν_{11} differs for solution-grown and melt-crystallized polymer, it being known that different kinds of folds are present in these two cases,³⁰ implies that the relative orientation of adjacent chains in the unit cell is correlated. That is, a chain reentering the crystal from a fold surface is not independent of its emerging portion: it "knows where it came from." This would not be likely if the fold were "loose," that is if there were enough methylene groups in it so that it possessed almost complete conformational flexibility. In such a case the reentrant chain could adapt to the packing requirements of the lattice and not be hindered by the special conformational restrictions imposed by the structure of the fold. This "loose" fold characteristic appears not to be supported by the experimental observations, and we are therefore led to the concept of a "tight" fold. The comparability of the half-widths of ν_{11} for all samples of high-density polyethylene also suggests uniformity in the fold structure. Thus, although we cannot specify the nature of the fold structure in detail, we believe it must be "tight" in the sense discussed above.

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³¹ P. J. Flory, J. Am. Chem. Soc. **84**, 2857 (1962).