

INTERFERENCE DISTORTION OF THE 73 cm^{-1} ABSORPTION LINE IN POLYETHYLENE

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Abstract—The decrease of the absorption strength of the 73 cm^{-1} line in polyethylene and the strong antiresonance occurring above 310 K at the high frequency side of the line are explained by assuming a Fano type coupling between the 73 cm^{-1} phonon and a continuum of infrared active vibrational modes. The parameters determining the line shape are deduced from experimental absorption curves and conceivable coupling mechanisms are discussed.

INTRODUCTION

Polyethylene (PE) is a nonpolar partially crystalline polymer. In the far-infrared spectral region PE shows at room temperature a strong absorption line at 73 cm^{-1} and a weak line at 108 cm^{-1} due to optical phonons in the crystalline portions of the material.⁽¹⁾ Both lines are superimposed on a continuous background absorption. Recent investigations revealed that the absorption strength of the 73 cm^{-1} line decreases with rising temperature and that above about 310 K the line becomes asymmetric with a pronounced antiresonance at its high frequency wing.⁽²⁾

The strong antiresonance suggests an explanation according to Fano's treatment of interference distortion of atomic transition.⁽³⁾ Similar effects have also been found for various interacting excitations in solids.^(4,5) The measurements shown in Fig. 1 represent the first observation of a Fano type antiresonance in a polymer. Basically the line shape of a transition between discrete energy levels may be disturbed by interference of the states of the discrete spectrum with those of a continuous spectrum.

THEORY

For polyethylene we assume that the amplitude X_0 of the optical phonon yielding the 73 cm^{-1} line is linearly coupled with the amplitudes X_μ of an infrared active continuum of vibrational modes. This continuum is at least partially responsible for the continuous background absorption. The dynamical equation of the coupled phonons driven by an external electric field E has the form

$$\begin{aligned}(\omega_0^2 - \omega^2 - i\omega\gamma_0)X_0 + \sum_{\mu} L_{0\mu}X_{\mu} &= Z_0E \\ L_{\mu 0}X_{\mu} + (\omega_{\mu}^2 - \omega^2 - i\epsilon)X_{\mu} &= Z_{\mu}E\end{aligned}\quad (1)$$

where Z_0 and Z_{μ} are suitably normalized effective charges,⁽⁶⁾ $L_{0\mu} = L_{\mu 0}$ are phenomenological coupling coefficients being generally complex and the other terms have their usual meanings. The optical absorption coefficient $\alpha(\omega)$ of the coupled system can easily be determined. It is found that $\alpha(\omega)$ decomposes into two additive contributions

$$\alpha(\omega) = \alpha_c(\omega) + \alpha_d(\omega)\quad (2)$$

where $\alpha_c(\omega)$ gives the absorption of the continuous background and $\alpha_d(\omega)$ is due to the discrete optical phonon renormalized by the mode coupling. In the limit $\epsilon \rightarrow 0$, for $\alpha_c(\omega)$ the well known result⁽⁷⁾ is obtained:

$$\alpha_c(\omega) = \frac{4\pi\omega}{nc} \text{Im} \sum_{\mu} Z_{\mu}^2 (\omega_{\mu}^2 - \omega^2 - i\epsilon)^{-1}\quad (3)$$

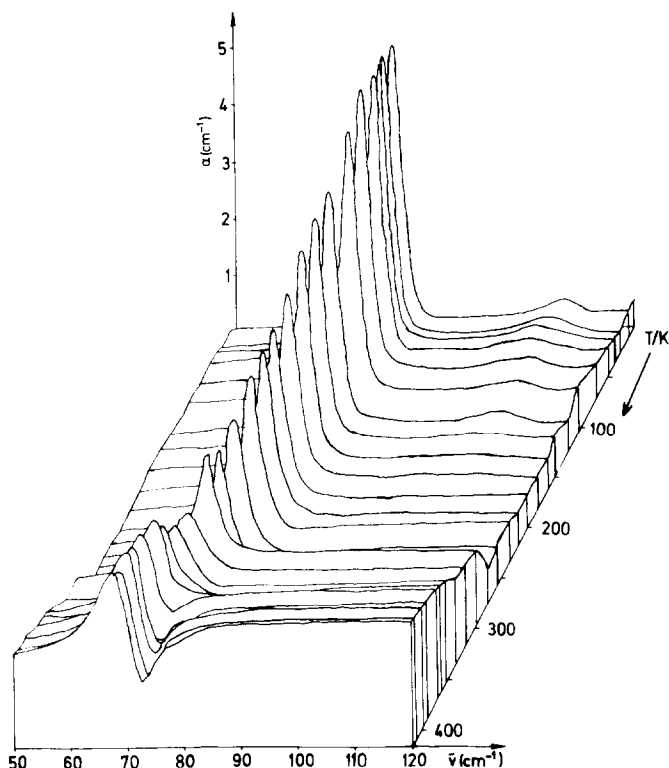


Fig. 1. Far-infrared absorption spectra of PE (6011 L) at various temperatures (after Ref. 2).

with $\epsilon \rightarrow 0$, we obtain

$$\alpha_c(\omega) = \frac{2\pi}{nc} Z^2(\omega) D(\omega)$$

where n is the refractive index and c the speed of light. The index μ of Z_μ has been replaced by the continuously varying frequency ω . Then $D(\omega)$ is the density of states of the continuum modes. For $\alpha_d(\omega)$ we get:

$$\alpha_d(\omega) = \alpha_d^{(0)} [1 + W(\Omega_0^2 - \omega^2)/(\omega\Gamma_0)] / [1 + (\Omega_0^2 - \omega^2)^2/(\omega\Gamma_0)^2] \quad (4)$$

with

$$W = 2A''(A' - Z_0) / [(Z_0 - A')^2 - A''^2]$$

$$\alpha_d^{(0)} = 4\pi[(Z_0 - A')^2 - A''^2] / nc\Gamma_0$$

and

$$\Omega_0^2 = \omega_0^2 - \Delta', \quad \omega\Gamma_0 = \omega\Gamma_0 + \Delta''$$

where

$$A = A' + iA'' = \sum Z_\mu L_{0\mu} (\omega_\mu^2 - \omega^2 - i\epsilon)^{-1}$$

$$\Delta = \Delta' + i\Delta'' = \sum L_{0\mu}^2 (\omega_\mu^2 - \omega^2 - i\epsilon)^{-1}$$

The coefficient W yields the antiresonance. Therefore W may be regarded as an asymmetry parameter; W vanishes if $A'' = 0$. This shows that the occurrence of an antiresonance requires the mode coupling ($L_{0\mu} \neq 0$) as well as the infrared absorption ($Z_\mu \neq 0$) of the coupled continuum of vibrational modes. Ω_0 and Γ_0 are the renormalized resonance frequency and the damping constant of the discrete phonon, respectively. The parameter $\alpha_d^{(0)}$ represents the absorption strength. It may be modified by the mode

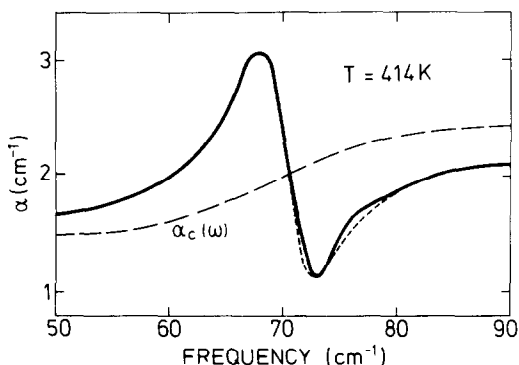


Fig. 2. Absorption coefficient $\alpha(\omega)$ at 414 K. Continuous line: experimental curve; broken line: fitted curve; $\alpha_c(\omega)$: hypothetical background absorption.

coupling even if the absorption line remains symmetric with $W = 0$. The depth of the antiresonance is limited by the thermodynamic requirement $\alpha = \alpha_c + \alpha_d > 0$. This implies the upper boundary for the magnitude of the asymmetry parameter $|W| < 2\alpha_c/\alpha_d^{(0)}$. Further we note that in the limit $\Gamma_0 \ll \Omega_0$, equation (3) may be rewritten in the form of the well known Fano line shape formula.^(3, 5)

EXPERIMENTAL RESULTS

We have fitted the absorption curves of Fig. 1 according to equations (2) and (4) assuming Ω_0 , Γ_0 , $\alpha_d^{(0)}$ and W to be independent of frequency in the vicinity of the resonance. At temperatures above 300 K the asymmetric absorption band extends over a frequency range, where the background absorption shows a considerable frequency variation which cannot be experimentally determined. Therefore we had to specify a frequency dependent absorption coefficient α_c in order to obtain a reasonable agreement between the experimental and fitted curves. Figure 2 shows a typical fitted absorption curve with the hypothetical continuous absorption α_c . The renormalized resonance frequency Ω_0 and the damping Γ_0 as functions of temperature determined by this fitting procedure are given in Fig. 3 and the results for $\alpha_d^{(0)}$, W and $\alpha_c(\Omega_0)$ are shown in Fig. 4. The coupling between the discrete phonon and the phonon continuum sets in at approximately 80 K and increases in strength with rising temperature. This is indicated by the continuous decrease of $\alpha_d^{(0)}$ and the frequency Ω_0 above 80 K. Up to 310 K the line shape is symmetric. Thus $W = 0$ and $A = A'$ is real below this temperature. Also Δ'' is very small up to 290 K, which can be seen from the only slightly increasing damping constant Γ_0 . Around 300 K the situation changes drastically. The background absorption α_c rises within 10 K to twice its lower temperature value. In the same temperature range Γ_0 increases and the line shape becomes asymmetric. Thus

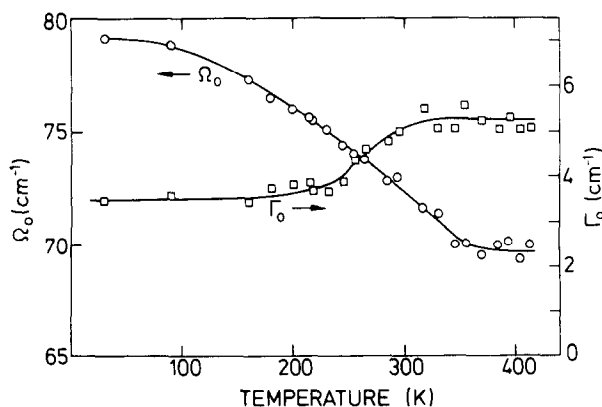


Fig. 3. Resonance frequency Ω_0 and damping constant Γ_0 as functions of temperature.

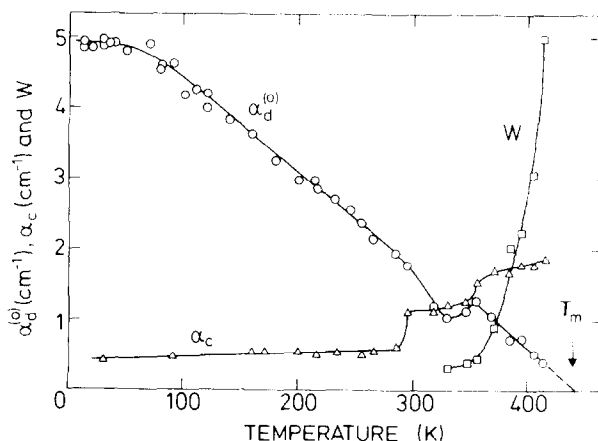


Fig. 4. Absorption strength $\alpha_d^{(0)}$, asymmetry parameter W and background absorption $\alpha_c(\Omega_0)$ as functions of temperature: T_m is the melting temperature of crystalline PE.

A is now complex with $A'' < 0$ yielding a positive asymmetry parameter $W (A' < Z_0)$. When the temperature is further raised, W increases strongly and the absorption strength $\alpha_d^{(0)}$ may be extrapolated to zero at about the melting temperature $T_m = 430$ K of crystalline PE.

DISCUSSION

The coupling mechanism of the discrete phonon of 73 cm^{-1} to a continuum of infrared active modes introduces the question for the physical nature of this continuum. We discuss two conceivable mechanisms:

- The PE crystallites with an mean edge-length of $300\text{--}500\text{ \AA}$ contain crystal defects of several species. Here the most important and at the same time the simplest one is the so called 'kink'-defect formed by two neighboured gauche positions of three successive CH_2 groups.^(1,8) Because of the relaxation of the k -selection rule, such defects contribute to some extent to the continuous background absorption. This has been proved by investigating annealed material. Annealing lowers the number of defects in the crystallites and always reduces the background absorption. However, a strong influence of the kinks on the temperature behaviour of the line distortion is unlikely, since the concentration of kinks between room temperature and the melting point does not vary remarkably.⁽⁹⁾
- The continuum of vibrational modes of the amorphous parts of the material must also be taken into account. Again due to the lack of translational symmetry all modes of the amorphous parts are infrared active.⁽⁷⁾ The coupling mechanism may be given by the transition of chains from the crystallite surfaces in a distance of $\sim 5\text{ \AA}$ corresponding to the b -axis length of the crystal. The similarity of the mean chain distance in the amorphous parts to the b -axis value can explain the observed fact, that the band intensity of the 73 cm^{-1} band is so much stronger than that of the 108 cm^{-1} ,⁽²⁾ an experimental observation having no stringent explanation up to now. From symmetry relations the two bands corresponding to two transversal vibrations in b -axis direction (73 cm^{-1} , B_{1u}) and a -axis direction (108 cm^{-1} , B_{2u}) should not vary drastically in their absorption intensity. If we assume that the effective charge of the discrete phonon of 73 cm^{-1} Z_0 is equal or close to zero, then the effect would still exist (see equation 4), since A' would produce a 'transfer' of absorption strength from the continuum to the discrete phonon. By coupling via the b -axis this would only be the case for the 73 cm^{-1} phonon and not for the 108 cm^{-1} mode.

In order to gain a complete understanding of the microscopic phonon processes in PE additional experiments are necessary. In particular materials with different crystal-

linity should be investigated. Furthermore other partially crystalline polymers are interesting, because it is very probable that phonon interactions of the type discussed here are not restricted to PE.

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