

phases, as did earlier work for the α phase within this pressure range.^{3,4} However we find a strong temperature dependence for the pressure coefficient which, in the theory of Benedek, Bloembergen, and Kushida,³ is evidence that the variation of intermolecular bonding with intermolecular distance is an important factor in both the pressure and the temperature dependence of the resonance frequency. Our measurements to date give the following coefficients (kc per 1000 psi, all ± 0.2): α and β phases, 2.6 at 29°C; α and γ phases, 1.5 at 0°C; α phases -0.5 at -76°C; γ phase +0.1 at -76°C.

Work is continuing on these measurements, and an x-ray and nuclear resonance single crystal analysis of the structure is in progress in these laboratories.

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Infrared Spectra of Polyethylene and Long Chain *n*-Paraffins

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OBSERVATIONS of the infrared spectra of some highly crystalline, unbranched polyethylene and long chain normal paraffins, together with an examination of the rather extensive literature on this subject, indicate that several very puzzling situations exist.

According to the usual interpretation of the very long paraffin-crystal spectrum on the basis of a model having a factor group isomorphous with V_h , the infrared spectrum should exhibit two CH stretching mode doublets, a CH₂ bending mode doublet and a CH₂ rocking mode doublet all having perpendicular dichroism (with respect to the carbon chain axis). In addition there should occur a single CH₂ wagging mode band and possibly a CH₂ twisting mode singlet of parallel dichroism.¹ The perpendicular bands have all been assigned unambiguously and offer no difficulty.² However, no parallel band can reasonably be assigned as a fundamental. Four bands are observed³ in the region where the CH₂ wagging fundamental is expected, namely at 1310, 1355, 1370, and 1380 cm⁻¹. The first three must be due to the amorphous part of the polyethylene since their intensity increases very greatly upon melting and they are absent in the spectra of very long *n*-paraffins which form perfect crystals. This is very clearly evidenced in the spectrum of amorphous and crystalline polyethylene wax obtained by M. B. Hall and shown in the paper by Nichols.³ The remaining band at 1380 cm⁻¹ is due to the symmetric-deformation mode of the terminal methyl groups. The possibility of overlapping here is excluded, since the spectrum of a very long chain unbranched polyethylene* shows no absorption at this wavelength.

The apparent absence (or extremely low intensity) of the CH₂ wagging fundamental in polyethylene is quite unexpected for the following reasons. In both the wagging and rocking modes of vibration, the distortion of the four carbon bonding orbitals is geometrically the same. Since the four orbitals are approximately equivalent, it follows that the change in dipole moment for the wagging vibration would be nearly equal to that for a rocking vibration of the same amplitude. The mean square amplitude of the normal wagging mode is approximately one-half that of the

rocking mode at 720 cm⁻¹, using the formula $\langle x_n^2 \rangle = \frac{h}{8\pi^2 c v_n} \coth \frac{h c v_n}{2kT}$, where ν_n is the vibrational frequency in wave numbers.⁴ It, there-

fore, would be surprising if the rocking vibration intensity were more than an order of magnitude greater than that of the wagging mode. Since the observed spectra indicate that the discrepancy is much greater than this the situation must be considered anomalous.

The nonappearance of a parallel absorption-band which can be attributed to CH₂ twisting is not troublesome however, since in the approximation of isolated molecules (correlating the spectrum with the line group rather than the space group, reference 1) this vibration is inactive and its intensity is expected to be very low.

Another difficulty in the spectral interpretation of paraffin crystals arises in connection with the well-known band series of uniformly spaced, sharp absorptions in the region 1180-1300 cm⁻¹. These bands are found with considerable intensity in certain long chain fatty acid crystals and other crystals containing long CH₂ sequences.⁵ They are also observed in *n*-paraffin crystals with greatly reduced intensity. These bands have been commonly attributed to CH₂ wagging and/or CH₂ twisting.^{5,6} This hypothesis would seem to be untenable on the basis of the spectrum obtained by Cole and Jones⁷ of a single crystal of eicosanoic acid wherein the strong, sharp 1180-1300 cm⁻¹ band series shows a polarization the same as the component of the CH₂ rocking vibration at 720 cm⁻¹; i.e., perpendicular to the carbon chain rather than parallel as would be required for either the wagging or twisting mode.

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* Marlex 50, commercial polyethylene produced by Phillips Petroleum Company.

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⁶ Primas and Günthard, *Helv. Chim. Acta*, **36**, 1659, 1791 (1953).

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Fluorescence Spectrum of Am²⁺ in LaCl₃†

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IT is now well recognized that 5f electrons occur in the ground-state configurations of atoms and ions of the actinide elements.¹

Fluorescence is well known in a number of lanthanide ions where it occurs because of the presence of 4f electrons. By analogy, one would expect to observe fluorescence in some actinide ions.

Fluorescence has not been observed in neptunium or plutonium compounds.² We wish to report here the first observation of the Am²⁺ fluorescence spectrum.

Single crystals of LaCl₃ (m.p. 860°C) containing 0.04 (sample I) and 0.20 (sample II) mole percent Am²⁺ were grown by the Stockbarger method.

The fluorescence is self-excited at room temperature owing to the radioactivity of Am²⁴¹. For the observation of the fluorescence spectrum however, a 1000 w AH-6 mercury lamp was employed. The spectrum was photographed on a Jarrell-Ash 21-ft Wadsworth mount spectrograph using a 15 000 lines/in. grating and a 400 μ slit with exposure times of 3 to 9 hr. The dispersion of the instrument is about 5 \AA /mm. Spectra were taken at room temperature and at liquid-nitrogen temperature.

All of the lines observed in the fluorescence spectrum are listed in Table I together with their visually estimated intensities. Lines marked with an asterisk coincide exactly with lines found in the absorption spectrum, and may be assumed to represent transitions from excited electronic states to the ⁷F₀ level of the ground-state multiplet. The Am²⁺ fluorescence spectrum shows somewhat different behavior in this respect from its analog Eu²⁺. In the former, we have observed fluorescence arising from four relatively low-lying excited electronic levels whereas in the latter fluorescence is observed only from the two lowest-lying electronic levels above the ⁷F ground-state multiplet.³