

tensiometric cell; (3) by the form of the oscillographic recordings of the voltage output of the tensiometric cell, when the electrolysis cell is submitted to short rectangular current pulses.

The practical absence of "exchange overvoltage" appears thus to be a quite general property at high enough temperature, and with melted chloride baths, not only for metals whose electrochemical behavior with aqueous solutions is "normal," but also for intermedium and inert ones, and moreover when these metals are in the solid state.

Recent researches from this Laboratory confirm this conclusion also for electrodes of the type: Mg/KCl+MgCl₂ at 550°C, and Al/AlCl₃+NaCl at 200°C.²

On the other hand, the experiments referred to, give clear evidence of occurring anodic passivity phenomena also with melted electrolytes, as a consequence of the presence or formation on the electrode surface of covering layers.

These layers may consist: (1) of oxides or oxichlorides formed by spontaneous reaction or by anodic process when the baths are not carefully purified from the last traces of water; (2) of oxides formed on the metal surface previous to the introduction of the metals in the cells; (3) of the chloride of the electrode metal, when in a multicomponents bath an oversaturation condition in respect to this salt has been attained at the electrode surface.

The analogy between these phenomena and the well-known ones, observed with aqueous solutions, is made clearer by the intervening of instability and oscillatory conditions also with melted salts.

The passivity of Mg electrodes disappears by heating to the melting point of Mg.

* The researches reported in this paper have been sponsored in part by the Air Research and Development Command U. S. Air Force, under Contract No. AF 61(514)733 C through the European Office, ARDC, G. Sternheim and M. Francini wish to express their gratitude to the A. Tonolli e C. Co. of Milan for a grant in aid.

¹ Pontelli, Rivolta, and Montanelli, *Z. Elektrochem.* 59, 64 (1955); R. Pontelli and G. Montanelli, *J. Chem. Phys.* 22, 1981 (1954); R. Pontelli and G. Sternheim, *J. Chem. Phys.* 23, 1358, 1971 (1955); R. Pontelli, *Z. Elektrochem.* 59, 778 (1955); R. Pontelli and G. Montanelli, *Alluminio* (to be published); and Pontelli, Sternheim, Manocha, and Francini, *Rend. ist. lombardo sci.* (to be published).

² The absence of exchange overvoltage for the electrode: solid Al/AlCl₃+NaCl is interesting also in view of the nature of chemical bonds in AlCl₃.

Note on Vibrations of Linear Chains of Particles

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(Received March 5, 1956)

A PROBLEM of fundamental importance in the interpretation of vibrations of certain types of crystals and molecules is that of the longitudinal normal vibrations of a linear chain of N identical masses m with free ends. The solution of this problem for nearest neighbor coupling with force constant K is simplified and systematized by the choice of an x -axis with its origin at the center of the equilibrium configuration. This procedure, in contrast with the usual one of placing the coordinate origin at an end of the chain, enables one to utilize symmetry considerations to maximum extent. If x_n denotes the equilibrium position of the n th particle ($n=1$ at one end of the chain and $n=N$ at the other end), $d=x_n-x_{n-1}$ and q_n denotes its small displacement from equilibrium during the r th normal mode, then $q_n=A_{nr}\cos(\omega_r t-\beta_r)$ where $\omega_r=(4K/m)^{1/2}\sin(r\pi/2N)$ if $r=1,2,\dots,N-1$ and $A_{nr}=A_r^0\cos(r\pi x_n/Nd)$ for even r or $A_{nr}=A_r^0\sin(r\pi x_n/Nd)$ for odd r . The value $r=0$ yields the zero-frequency translational mode and the values $r\geq N$ yield repetitions of the frequencies.

The addition of next-nearest neighbor coupling with force constant $k=\epsilon K$ to the above problem yields a model probably more nearly approximating the situation in a molecule or crystal. The resulting problem can be readily solved by the usual methods for normal modes if N is less than 7. The general problem, for N arbitrary, can be investigated by successive approximations if one takes as the zero-order approximation the corresponding

problem with nearest-neighbor coupling, namely, the case $\epsilon=0$. Calculations of this kind show that the solutions tend for large N toward the form, $q_n=A_{nr}\cos(\omega_r t-\beta_r)$, with $\omega_r=(4K/m)^{1/2}\{\sin^2(r\pi/2N)+\epsilon\sin^2(r\pi/N)\}^{1/2}$ if $r=1,2,\dots,N-1$ and $A_{nr}=A_r^0\cos(r\pi x_n/Nd)$ for even r or $A_{nr}=A_r^0\sin(r\pi x_n/Nd)$ for odd r .

Icosahedral Coordination Number 12

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IT is well known that for a coordination number of 8 the cubic arrangement, which occurs in many crystals and for which the critical radius ratio, ρ , is 0.732, is less favorable than the square antiprism arrangement for which $\rho=0.645$.¹ For a coordination of 12 an arrangement based on a close packing of spheres which possesses a ρ of 1.00, such as the cubo-octahedron, has been cited. It appears not to be generally recognized that a coordination figure with the centers of twelve spheres at the vertices of a regular icosahedron gives a more favorable packing arrangement. Each of the outer spheres is tangent to five outer spheres in contrast to four for each sphere of the cubo-octahedron. In addition, ρ for the icosahedral coordination is 0.902.

Hunt, Rundle, and Stosick² determined by means of x-ray diffraction that in the compound, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, two sets of lanthanum ions had coordination numbers of 9 and 12, respectively. Because heavier lanthanum sulfates failed to crystallize with this structure they considered the radius of a lanthanum ion to be barely able to support the coordination of 12 oxygens. An examination of the packing about the 12-coordination lanthanum shows that it is indeed approximately a regular icosahedron.

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

¹ A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1956), second edition, p. 90; L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948) second edition, p. 381.

² Hunt, Rundle, and Stosick, *Acta Cryst.* 7, 166 (1954).

Polymorphism of Para-Dichlorobenzene*

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A LARGE shift in the pure quadrupole resonance frequency has given evidence for a third crystal structure (γ) in samples of para-dichlorobenzene containing one or two mole percent of para-xylene or a few percent of benzene. Throughout the range in which it has been observed (-76° to $+10^\circ\text{C}$), the resonance frequency for this phase remains approximately 430 kc higher than that for the normal room temperature phase (α) at the same temperature, whereas in both α and the high temperature phase (β) the resonance frequencies of these doped samples agree with those for the corresponding phases of pure para-dichlorobenzene.¹

The γ phase was first detected briefly some time ago by the appearance of this new resonance in a single crystal of pure para-dichlorobenzene while it was accidentally subjected to severe strain.² Although we have now produced it in a small portion of a pure polycrystalline sample crushed in a crude fashion between two pistons and cooled by dry ice, we have been unable to convert more than a small portion of a pure sample to the γ phase by hydrostatic pressures up to 8000 psi, applied while the sample was at -76°C . However it appears that the phase produced by a pressure of 1600 atmos at 24.8°C , which was recently announced,³ is the same structure, since the quadrupole resonance frequencies lie in the same region.

Our measurements at up to 8000 psi show a linear pressure dependence for the resonance frequency in each of the three

phases, as did α and β range.^{3,4} However the pressure coefficients for α , β , and γ are different, and the molecular bond length factor in both α and β the resonance frequency following coefficient 2.6 at 29°C ; α and γ phase $+0.1$ at 29°C .

Work is continuing on the nuclear resonance progress in these

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¹ C. Dean and R. E. Rundle, *Phys. Rev.* 102, 102 (1956).
² C. Dean, thesis, University of Pittsburgh, 1956.
³ Benedek, Bloembergen, and D. Dautrepeau, *Phys. Rev.* 102, 102 (1956).

⁴ D. Dautrepeau, *Phys. Rev.* 102, 102 (1956).

Infrared

Natural

OBSERVATIONS of crystalline, paraffins, together with the literature on this situation exist.

According to the crystal spectrum, isomorphous with CH stretching mode, CH₂ rocking mode (with respect to the CH₂ stretching mode singlet) have all been assigned. However, no paraffin has been assigned. Four bands waggling fundamental and 1380 cm⁻¹. The of the polyethylene upon melting and paraffins which are detected in the spectrum wax obtained by N. The remaining bands deformation mode of overlapping here chain unbranched length.

The apparent waggling fundamental the following reason vibration, the dist geometrically the equivalent, it follows waggling vibration vibration of the of the normal waggling rocking mode at 720 where ν_n is the vibration

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.

* Work done in the Sarah Mellon Seale Radiation Laboratory and supported by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

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‡ C. Dean and R. V. Pound, J. Chem. Phys. 20, 195 (1952).

§ C. Dean, thesis, Harvard, 1952 (unpublished).

|| Benedek, Bloembergen, and Kushida, Bull. Am. Phys. Soc. Ser. II, 1, 11 (1956).

¶ D. Dautreppe and B. Dreyfus, Compt. rend. 241, 795 (1955).

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

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(Received February 20, 1956)

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 $\langle x_n^2 \rangle = \frac{h}{8\pi^2 c \nu_n} \coth \frac{h \nu_n}{2kT}$, 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.

¹ Marvin C. Tobin, J. Chem. Phys. 23, 891 (1955).

² Brown, Sheppard, and Simpson, Discussions Faraday Soc. 9, 261 (1950).

³ J. B. Nichols, J. Appl. Phys. 25, 840 (1954).

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

⁴ R. W. James, Physik. Z. 33, 737 (1932).

⁵ Jones, McKay, and Sinclair, J. Am. Chem. Soc. 74, 2575 (1952).

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

⁷ A. R. H. Cole and R. N. Jones, J. Opt. Soc. Am. 42, 348 (1952).

Fluorescence Spectrum of Am³⁺ in LaCl₃†

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(Received February 20, 1956)

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 Am³⁺ fluorescence spectrum.

Single crystals of LaCl₃ (m.p. 860°C) containing 0.04 (sample I) and 0.20 (sample II) mole percent Am³⁺ 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 400μ slit with exposure times of 3 to 9 hr. The dispersion of the instrument is about 5 Å/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 Am³⁺ fluorescence spectrum shows somewhat different behavior in this respect from its analog Eu³⁺. 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