

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:  $Mg/KCl+MgCl_2$  at  $550^\circ C$ , and  $Al/AlCl_3+NaCl$  at  $200^\circ C$ .<sup>2</sup>

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.

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

<sup>2</sup> The absence of exchange overvoltage for the electrode: solid  $Al/AlCl_3+NaCl$  is interesting also in view of the nature of chemical bonds in  $AlCl_3$ .

### 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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(Received February 20, 1956)

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,  $\rho$ , is 0.732, is less favorable than the square antiprism arrangement for which  $\rho=0.645$ .<sup>1</sup> For a coordination of 12 an arrangement based on a close packing of spheres which possesses a  $\rho$  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,  $\rho$  for the icosahedral coordination is 0.902.

Hunt, Rundle, and Stosick<sup>2</sup> determined by means of x-ray diffraction that in the compound,  $La_2(SO_4)_3 \cdot 9H_2O$ , 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.

<sup>1</sup> A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950), second edition, p. 90; L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948) second edition, p. 381.

<sup>2</sup> Hunt, Rundle, and Stosick, *Acta Cryst.* 7, 166 (1954).

### Polymorphism of Para-Dichlorobenzene\*

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(Received February 24, 1956)

A LARGE shift in the pure quadrupole resonance frequency has given evidence for a third crystal structure ( $\gamma$ ) 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 ( $-76^\circ$  to  $+10^\circ C$ ), the resonance frequency for this phase remains approximately 430 kc higher than that for the normal room temperature phase ( $\alpha$ ) at the same temperature, whereas in both  $\alpha$  and the high temperature phase ( $\beta$ ) the resonance frequencies of these doped samples agree with those for the corresponding phases of pure *para*-dichlorobenzene.<sup>1</sup>

The  $\gamma$  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.<sup>2</sup> 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  $\gamma$  phase by hydrostatic pressures up to 8000 psi, applied while the sample was at  $-76^\circ C$ . However it appears that the phase produced by a pressure of 1600 atmos at  $24.8^\circ C$ , which was recently announced,<sup>3</sup> 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 a range.<sup>3,4</sup> However, the pressure coefficients, and Ku molecular bonding factor in both the resonance following coefficient 2.6 at  $29^\circ C$ ;  $\alpha$  and  $\gamma$  phase  $+0.1$  at.

Work is continuing nuclear resonance progress in these

\* Work done in part reported by the U. S. Air Research and Development Command, Ames, Iowa.

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<sup>1</sup> C. Dean and R. E. Rundle, *J. Chem. Phys.* 24, 1000 (1956).

<sup>2</sup> C. Dean, thesis, Iowa State College, Ames, Iowa, 1955.

<sup>3</sup> Benedek, Bloembergen, and D. Dautreppe, *J. Chem. Phys.* 24, 1000 (1956).

<sup>4</sup> D. Dautreppe and R. E. Rundle, *J. Chem. Phys.* 24, 1000 (1956).

### Infrared

Naval

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

According to the crystal spectrum, isomorphous with CH stretching mode  $CH_2$  rocking mode (with respect to the CH stretching mode) have all been assigned. However, no paraffin. Four bands waggling fundamental and  $1380\text{ cm}^{-1}$ . The of the polyethylene upon melting and paraffins which are detected in the spectrum wax obtained by M. 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 of the of the normal waggling rocking mode at  $720\text{ cm}^{-1}$  where  $\nu_n$  is the vibrational frequency.