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## Dependence on Atomic Number of the Diamagnetic Susceptibility Calculated from the Thomas-Fermi-Dirac Model

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THE molar diamagnetic susceptibilities<sup>1</sup> in units of  $10^{-6}$  cm<sup>3</sup>

$$\chi_{\text{mole}} = -0.79233(Z-n)\langle(r/a_0)^2\rangle$$

have been computed for free neutral atoms ( $n=0$ ) and free  $n$ -ply ionized positive ions ( $n=1$  to 4) on the IBM 607 from the TFD charge distributions, recently published by one of us.<sup>2</sup> The full numerical results are available on request. The dependence of  $\chi$  on  $Z$  obtained is shown in Fig. 1. Our numerical values are listed

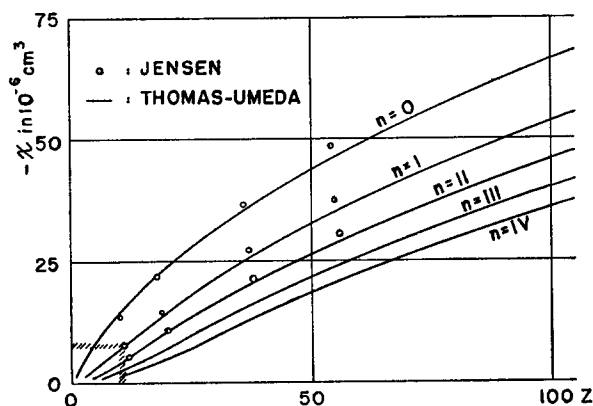


FIG. 1. The dependence on atomic number of molar diamagnetic susceptibilities for free neutral TFD atoms and free singly through quadruply ionized ions. The shaded part is shown in Fig. 2.

in Table I<sup>3</sup> for the inert gas atoms and the ions homologous to inert gases, which furnish the only comparable experimental values. The deviations from the values previously given by Jensen<sup>4</sup> may be due to his partial treatment of exchange effects, and seem to reduce the discrepancy with the experimental data.

As seen from Fig. 2, with an expanded scale, it is characteristic of the TFD theory, although this is rather of mathematical than of physical interest, that the  $\chi$  curve for neutral atoms is distinctly steeper than those for ions, which are very alike, and finally runs into the origin tangentially to the  $Z$ -axis, while in the TF theory it

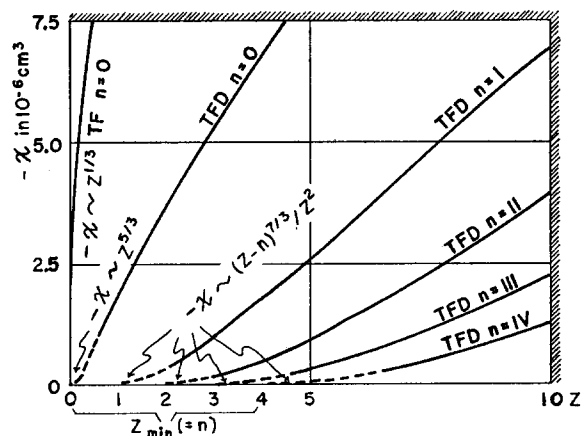


FIG. 2. Characteristic behavior of the  $\chi$  curve for neutral TFD atoms in comparison with those for neutral TF atoms (e.g.,  $\chi(\text{TF}) = -9.43Z^2$ ) as well as singly through quadruply ionized TFD ions in the region of small values of the atomic number.

TABLE I. Molar diamagnetic susceptibility in units of  $10^{-6}$  cm<sup>3</sup>.

Ne	14.33	Ar	22.15	Kr	35.51	Xe	45.96
Na <sup>+</sup>	7.83	K <sup>+</sup>	14.04	Rb <sup>+</sup>	25.53	Cs <sup>+</sup>	34.92
Mg <sup>++</sup>	5.24	Ca <sup>++</sup>	10.26	Sr <sup>++</sup>	20.27	Ba <sup>++</sup>	28.79
Al <sup>+++</sup>	3.81	Sc <sup>+++</sup>	7.99	V <sup>+++</sup>	16.82	La <sup>+++</sup>	24.62
Si <sup>++++</sup>	2.92	Ti <sup>++++</sup>	6.45	Zr <sup>++++</sup>	14.33	Ce <sup>++++</sup>	21.52

happens to turn perpendicularly due to its proportionality<sup>5</sup> to  $Z^1$ . This behavior is established as follows. Since for very small values of the atomic number ( $Z \rightarrow 0$  for neutral atoms and  $Z \rightarrow n$  for  $n$ -ply ionized ions) the TFD theory gives in the first approximation

$$\rho \approx \frac{Z}{4\pi\mu^3}\beta^3 \quad \text{or} \quad \frac{Z}{4\pi\mu^3}\left(1 - \frac{3}{2} \frac{x}{x_0}\right) / x^{\frac{1}{2}}$$

for neutral atoms ( $\beta \rightarrow \infty$ ) or  $n$ -ply ionized ions ( $\beta$  finite), respectively, and correspondingly<sup>6</sup>

$$x_0 \approx 6.81Z^{\frac{1}{3}} \quad \text{or} \quad 6.08[(Z-n)/Z]^{\frac{1}{3}},$$

we have the limiting formulas for  $\chi$  in units of  $10^{-6}$  cm<sup>3</sup>

$$\chi \approx -17.28Z^{\frac{5}{3}} \quad \text{or} \quad -22.97(Z-n)^{\frac{7}{3}}/Z^2.$$

Thus,  $(d\chi/dZ)_{Z=0}$  or  $(d\chi/dZ)_{Z=n}=0$ , but, due to the different exponents ( $5/3$  and  $7/3$ ), the limiting  $\chi$  curve for neutral atoms is less inclined than those for ions, which incline in turn more and more with increasing value of  $n$  due to the denominator, which takes the form  $[n + (Z-n)]^2$ . It should be noted that these formulas for ions hold for the TF ions also, because the value of  $\beta$  is not involved in this derivation. The second approximations match the curves obtained well.

\* On leave from Okayama University, Japan.

<sup>1</sup> All notations are used with the meaning usual in the TFD theory. The values of physical constants are taken from Cohen, DuMond, Layton, and Rollett, *Revs. Modern Phys.* **27**, 363 (1955).

<sup>2</sup> L. H. Thomas, *J. Chem. Phys.* **22**, 1758 (1954).

<sup>3</sup> This table is to be compared with Table 29 of P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949). Table 1 of T. Hirone, *Sci. Repts. Tohoku Univ.* **11**, 24, 264 (1935), and Table VIII of W. R. Wyers, *Revs. Modern Phys.* **24**, 15 (1952). (We are indebted to Professor Van Vleck for this reference.)

<sup>4</sup> H. Jensen, *Z. Physik* **101**, 141 (1936).

<sup>5</sup> P. Gombás, reference 3, Eq. (27, 3) and (27, 7).

<sup>6</sup> This  $Z^{\frac{1}{3}}$  variation for neutral atoms was previously noted in the numerical results by one of us, K. Umeda, *J. Fac. Sci. Hokkaido Univ.* **11**, 3, 171 (1942), Eq. (22).

## Overvoltages and Passivity in Melted Electrolytes

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THE investigations carried out in this Laboratory on the electrode overvoltages with melted electrolytes<sup>1</sup> have been extended to electrodes at which a solid metal, whose electrochemical behavior in aqueous solutions is "intermedium" (as for Cu), or "inert" (as for Ni), exchanges ions with a bath of fused chlorides.

Let us consider the "apparent overvoltages," obtained under conditions allowing a strict control of the nature of the electrode processes and the practical elimination of the concentration overvoltage.

These apparent overvoltages are then comprehensive of those involved in the exchanges at the electrode surface and of the ohmic drop in the bath layer included in the tensiometric cell.

In the systems Ni/NiCl 10% to 20%+KCl 90% to 80% (weight percent), at 740°C; Cu/CuCl<sub>2</sub> (10%)+KCl (90%) at 740°C, the apparent overvoltages present pure ohmic character, as was found in preceding experiments with "normal" metals.

This is shown: (1) by the characteristics, which are linear and symmetric both on the anodic and the cathodic side; (2) by the law of dependence of the apparent overvoltage on the effective thickness and conductivity of the bath layer included in the

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<sub>2</sub> at 550°C, and Al/AlCl<sub>3</sub>+NaCl at 200°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.

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<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<sub>3</sub>+NaCl is interesting also in view of the nature of chemical bonds in AlCl<sub>3</sub>.

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  $\omega_r \doteq (4K/m)^{1/2} \{ \sin^2 \times (r\pi/2N) + \epsilon \sin^2(r\pi/N) \}^{1/2}$  if  $r=1, 2, \dots, N-1$  and  $A_{nr} \doteq A_r^0 \times \cos(r\pi x_n/Nd)$  for even  $r$  or  $A_{nr} \doteq A_r^0 \sin(r\pi x_n/Nd)$  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,  $\rho$ , 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,  $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , 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.

<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**, 106 (1954).

## 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

## Polymorphism of Para-Dichlorobenzene\*

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A LARGE shift in the pure quadrupole resonance frequency 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  $+10^\circ\text{C}$ ), 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  $-76^\circ\text{C}$ . However it appears that the phase produced by a pressure of 1600 atmos at  $24.8^\circ\text{C}$ , 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