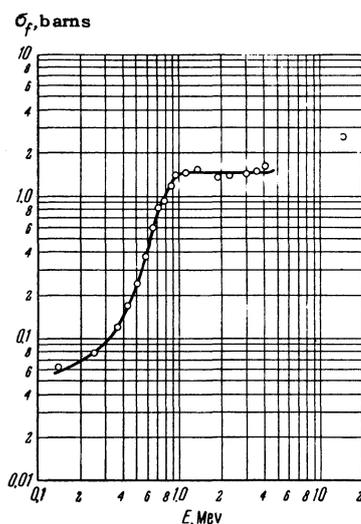


one. The source of fast neutrons of energy  $< 2$  Mev was the  $T(p, n)He^3$  reaction, those from 2 to 4 Mev were obtained from the  $D(d, n)He^3$  reaction, and those with energies of 15 Mev from the  $T(d, n)He^4$  reaction. The first reaction was produced in a van de Graaf generator, and the remaining two in a cascade generator. The fissions were counted in the two halves of the chamber both by fast and by thermal neutrons. Measurements with thermal neutrons are essential to determine the ratio of the effective amounts of fissionable matter in the chambers. Thermal neutrons were obtained by moderating fast neutrons in a paraffin block. The cadmium-difference method was used to exclude the influence of resonant neutrons and of fast neutrons passing through the paraffin. An experimental check disclosed practically no screening of one layer by the other.

To determine the absolute value of the  $Pu^{240}$  fission cross section, we used the energy dependence of the  $Pu^{239}$  fission cross section, obtained by averaging the data of our latest investigations. The energy dependence of the  $Pu^{240}$  fission cross section is shown in the diagram.



The  $Pu^{240}$  fission cross section is  $1.50 \pm 0.15$  barns at the plateau and agrees with the results obtained by Dorofeev and Dobrynin<sup>1</sup> by measurements with neutrons from a Ra-Be source ( $1.40 \pm 0.15$  barns). The fission cross section obtained for 15-Mev neutrons was  $2.6 \pm 0.2$  barns.

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<sup>1</sup>G. A. Dorofeev and Iu. P. Dobrynin; *Атомная энергия* (Atomic Energy), No. 2, 10 (1957).

<sup>2</sup>Iu. S. Zamiatin, Приложение к журн. *Атомная энергия* (Atomic Energy Supplement) No. 1, 27 (1957).

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### DIAMAGNETISM AND INTERATOMIC BONDS IN MOLECULES AND NON-METALLIC CRYSTALS

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THE majority of magnetic investigations of diamagnetic substances has remained up to now practically useless for a study of the nature of interatomic binding forces. The method suggested by us to treat diamagnetism<sup>1</sup> enables one to approach this problem anew. In the present note we intend to show some possibilities and perspectives of this method in an application to diamagnetic molecules and non-metallic crystals.

It is known that the diamagnetic susceptibility  $\chi$  of molecules and non-metallic bodies, which is experimentally measured, can theoretically be written in the form<sup>2</sup>

$$\chi = \chi_d + \chi_p \quad (1)$$

$$= - (Ne^2/6mc^2) \sum \bar{r}_i^2 + 2N \sum | \langle n | \mu_z | 0 \rangle |^2 / (E_n - E_0).$$

Although the terms  $\chi_d$  and  $\chi_p$  are individually not invariant with respect to a transformation of the origin of coordinates, only their sum being invariant, they take on a unique physical meaning, if we take for each electron the center of gravity of the corresponding electron shell as the origin. The Langevin component  $\chi_d$  depends only on the dimensions of the electron shells. The Van Vleck component  $\chi_p$ , on the other hand, depends on the symmetry type of these shells and on their deformability; for atoms and spherically-symmetric shells  $\chi_p = 0$ . In this way  $\chi_p$  can be used as a source of interesting information about the structure of the electron shells.

Since there is no method to split  $\chi$  experimentally into  $\chi_d$  and  $\chi_p$  an estimate of  $\chi_p$  can only be performed by means of comparing  $\chi_d$  with  $\chi$ , if there is a reliable method to determine  $\chi_d$  independently for each given substance. Kirkwood<sup>3</sup>

has given by an approximate variational method an expression for the polarizability of atoms,

$$\alpha = (4/9ka_0) \left| \sum \bar{r}_i^2 \right|^2, \quad (2)$$

which enables us, by using (1), to connect  $\chi_d$  with the experimentally measured  $\alpha$ , i.e.,

$$\chi_d = -(Ne^2\alpha_0^{1/2}/4mc^2) \sqrt{k\alpha}. \quad (3)$$

In spite of the fact that expressions (2) and (3) were only derived for atoms, we see easily that this derivation can be extended to any polyatomic system built up out of more or less symmetrical electron shells, if in the summation over the different electrons we take for the coordinate origin for each electron the center of gravity of the corresponding shell and if we understand by  $\alpha$ ,  $\chi$ ,  $\chi_d$ , and  $\chi_p$  the averaged (over-all directions) values of these quantities. We have shown recently<sup>1</sup> that actually the relation (3) can be successfully applied both to ionic crystals and to complex organic molecules. It has been shown then that for those substances of this group for which the electronic shells can be assumed a priori to be sufficiently symmetric, i.e., for which  $\chi_p \approx 0$ , the values of  $\chi_d$  evaluated from (3) agree with the experimentally measured  $\chi$ .

If we now turn to polar crystals with ions known to be deformed such as, for instance, KCl, KBr, and KI, we see that  $\chi_p \times 10^6$  is equal to +1, +5.2, +8.8, respectively.

From dispersion theory it is known that  $\alpha$  is inversely proportional to  $(E_n - E_0)$ , like  $\chi_p$  in (1), so that in a number of closely similar substances  $\chi_p$  must change approximately parallel to  $\alpha$ . Indeed, for KCl, KBr, and KI,  $\alpha$  is equal to 4.33, 5.57, and  $8.1 \times 10^{-24}$ , respectively. In the above-mentioned paper<sup>1</sup> we have shown that  $\chi_p$  is appreciable in atomic groups (C=O, O=N=O, C=C, C≡C, and so on) in which the interatomic binding occurs through  $\pi$  electrons. A further study of this problem shows that the evaluated values of  $\chi_p$  for the groups N=O and O=N=O are practically coincident and agree with  $\chi_p$  for the  $\text{NO}_3^-$  ion in crystals. The values of  $\chi_p$  for the carbonyl group >C=O and the carbonate ion  $\text{CO}_3^{2-}$  also coincide exactly. In other words at each given moment only one of the equivalent bonds is actually a multiple one in the  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  ions, and also in the O=N=O group. This can be considered to be a direct confirmation of Pauling's hypothesis<sup>4</sup> that the bonds C-O and N-O in the  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  ions are only  $1/3$  of the time in a state of a double  $\pi$  bond and in the nitro-group only half of the time.

|      | $\chi_p \cdot 10^6$ | $\Delta E$ (ev) |      | $\chi_p \cdot 10^6$ | $\Delta E$ (ev) |
|------|---------------------|-----------------|------|---------------------|-----------------|
| Si   | 19.35               | 1.12            | InP  | 24.6                | 1.25            |
| Ge   | 29                  | 0.75            | InAs | 31.78               | 0.33            |
| GaP  | 27.54               | 2.28            | InSb | 48                  | 0.18            |
| GaAs | 38.14               | 1.35            | ZnS  | 25.3                |                 |
| GaSb | 56.6                | 0.67            |      |                     |                 |

A large value of  $\chi_p$  is observed in the semiconductor crystals given in the table which is explained by the strong spreading out of the valence electron shells. Following Krumhansl and Brooks<sup>5</sup> one can assume that  $(E_n - E_0)$  in semiconductors corresponds to the width of the forbidden band  $\Delta E$ . This apparently explains the fact that in a number of similar substances an increase in  $\chi_p$  goes parallel with an increase in  $\alpha$ .

The anomalously large polarization paramagnetism is apparently characteristic also for purely molecular semiconductors, of which the aromatic compounds are typical representatives.  $\chi_p \times 10^6$  is, for instance, equal to +15.4 for naphthalene, +20.8 for anthracene, +19.0 for phenanthrene, and +27 for naphthacine. One can therefore assume that also metal-organic compounds belong to the group of semi-conductors since for many of them one finds a very large value of  $\chi_p$ . For instance,  $\chi_p \cdot 10^6$  is equal to +20 for  $\text{Hg}(\text{CH}_3)_2$ , +37.8 for  $\text{Hg}(\text{C}_4\text{H}_9)_2$ , and +43.5 for  $\text{Pb}(\text{C}_2\text{H}_5)_4$ .

The examples given can serve to illustrate the magnetochemical study of interatomic binding forces in very diverse diamagnetic substances.

In conclusion I express my deep gratitude to a number of friends for critical remarks and especially to A. G. Samoilovich and L. L. Korenblit for valuable advice.

<sup>1</sup>Ia. G. Dorfman, Dokl. Akad. Nauk SSSR, **119**, 305 (1958), Soviet Phys. "Doklady" (in press); J. Phys. Chem. (U.S.S.R.) (in press).

<sup>2</sup>J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, 1932.

<sup>3</sup>J. G. Kirkwood, Physik. Z. **33**, 57 (1932).

<sup>4</sup>L. Pauling, The Nature of the Chemical Bond, Ithaca, 1945.

<sup>5</sup>J. A. Krumhansl and H. Brooks, Bull. Am. Phys. Soc. **1**, 117 (1956).