

Electronic Structures of Polyatomic Molecules and Valence. Magnetism of B_2H_6

In one of a series of articles under the above general title, begun in the *Physical Review* (1932-33) and hereafter to be continued in the *Journal of Chemical Physics*, it was stated that, on the basis of the method of molecular orbitals used in these articles, the interesting gas B_2H_6 is probably paramagnetic.¹ In one of the following articles in *J. Chem. Phys.* it will be shown that the structure of the molecule can probably be described by the electron configuration

$$(1s^2[\sigma_z]^2[\pi]^3)_2[\sigma_z+\sigma_z]^2,$$

in which the hydrogens in each BH_3 are bound to the B mainly by two $[\sigma_z]$ and three $[\pi]$ electrons, and the two B's are bound together mainly by the two $[\sigma_z+\sigma_z]$ electrons. The two latter may also contribute a little to the B-H bindings, and the six $[\pi]$ electrons more or less to the B-B binding.

If the interaction between the two $[\pi]^3$ groups should be strong, one could better write $[\pi+\pi]^4[\pi-\pi]^2$, using B_2H_6 orbitals instead of $[\pi]^3[\pi]^3$, using BH_3 orbitals. The types $[\pi+\pi]$ and $[\pi-\pi]$ are respectively bonding and antibonding for the boron-boron bond, and the whole group of six electrons would give a net bonding action between the two borons. In this case these six together with the two $[\sigma_z+\sigma_z]$'s are closely analogous to the eight electrons $(\sigma+\sigma)^2(\pi+\pi)^4(\pi-\pi)^2$,—usually written $\sigma^2\pi^4\pi^{*2}$ or $(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$,—which make the double bond in O_2 . This set of electrons would give rise to three low-energy states

3A_2 , 1E , 1A_1 closely analogous to the three low states ${}^3\Sigma_g^-$, ${}^1\Delta_g$, ${}^1\Sigma_g^+$ of O_2 , with 3A_2 lowest analogous to ${}^3\Sigma_g^-$ of O_2 . (It is assumed that the molecule has the symmetry D_3 , but symmetry D_{3h} or D_{3d} would give essentially the same states.) B_2H_6 should then be paramagnetic like oxygen.

More probably the interaction between the two $[\pi]^3$ groups is weak, in which case, it can be shown, B_2H_6 should have a group of six low-energy states 3A_2 , 1E , 1A_1 , 1A_1 , 3E , 3A_2 close together. Very likely a 3A_2 would still be the lowest as in the other limiting case, but even if this should not be true, a 3A_2 and a 3E state must lie sufficiently close to the lowest state to be considerably populated at room temperature and so to make B_2H_6 paramagnetic. Since paramagnetism is thus predicted in both limiting cases, the same prediction is very likely, although not certain, to hold good for intermediate cases. Since, however, the actual case is probably near the second limiting case, it may be predicted with some confidence that B_2H_6 is actually at least weakly, but probably strongly, paramagnetic. If, however, B_2H_6 should prove to be diamagnetic or only weakly paramagnetic at room temperature, it may be expected to become more strongly paramagnetic on raising the temperature.

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April 10, 1933.

¹ R. S. Mulliken, *Phys. Rev.* **41**, 756 (1932).

On the Plasticity of Crystals

A. Smekal¹ recently in a letter to *The Physical Review* is still advocating the idea that microscopic crevices are the essential cause of the peculiar mechanical and plastic behavior of rocksalt and crystals in general. Although conclusive evidence has repeatedly been brought forth by myself and other writers that Smekal's "imperfection" theory does *not* account for some of the most essential physical properties of crystals, his remarks in the mentioned letter require some comment.

In the first place the postulate of microscopic crevices does not account for the fact that the strength of good, pure crystals against gliding is consistently of the order of one-thousandth of what one would expect for ideal lattices. If the crevices are, as Smekal states, of an *accidental* nature and if they are therefore irregularly distributed and of various sizes, they will cause a *wide spread* in the values of the strength against slipping for different specimens. Furthermore, it is known that the more imperfect (deformed, contaminated) a crystal is, the more its strength approaches values which one would really expect for the ideal crystal; and the more perfect a crystal is experimentally the smaller is its strength as compared with the strength an ideal crystal should have. This paradoxical behavior of real crystals is therefore exactly contrary to Smekal's theory.

Secondly, Smekal's ideas *do not account* for the *fundamental fact*, that the strength against slipping at higher

temperature is *independent* of the temperature, retaining a constant finite value over a considerable range of temperatures until the crystal melts abruptly and the shearing strength drops to zero. If crevices determined the shearing strength it would vary greatly with temperature, because the thermal energy of the crystal is of the same order of magnitude as the potential energy changes involved in widening or closing the crevices by a deformation of the crystal. It is not permissible, as Smekal has done, to explain the invariance of the strength against temperature changes by comparing the thermal energy with the total energy of an atom in the crystal. Indeed the energy of deformation is only a very small fraction of the total potential energy and is therefore quite comparable with the total thermal energy. The "imperfection" theory also has never accounted for the fact that the strength against shear is strongly dependent upon temperature for low temperatures although it assumes a constant value for higher temperatures.

In the third place some of the phenomena, *predicted* by the theory of the secondary structure and found experimentally by Mr. Hasler, myself, A. Goetz, A. Straumanis and F. Bitter, are *inconsistent* with Smekal's postulate of "Lockerstellen" (regions of loosely bound atoms). These effects are the following ones. The theory of the secondary structure requires that the distribution of matter, or energy in a crystal be represented by a triple Fourier series with at least two periods or two lattice constants, d and

$D \gg d$ which are characteristic for the primary and the secondary structure, respectively. The theory claims in the first place that the spacing D of the secondary structure is essentially independent of the conditions under which the crystals are grown. This is actually true for the secondary patterns which have been observed on Bi, Cd, Zn and especially for the magnetic secondary structure on magnetized crystals of Fe and Ni as observed by F. Bitter. The theory in the second place predicted that etching or evaporation would attack first the atoms in the center of the secondary blocks. This has been verified also and proves conclusively that the observed secondary patterns *cannot* be systems of slip lines as Smekal thinks. If they were slip lines their higher energy content naturally would favor etching or evaporation, so that instead of obtaining definite (triangular, etc.) etching grooves a system of long grooves would result. The fact that the outlines of the patterns observed by us offer a considerably greater resistance against etching than the apparently ideal parts I regard as a conclusive confirmation of the postulate of a secondary structure.

Finally a powerful esthetic argument may be advanced against the theory that imperfections are the cause of all the structure-sensitive properties of crystals. Indeed during the ten years of its existence nobody has been able to derive from this theory *any quantitative* description of the structure-sensitive properties of crystals. The theory of the secondary structure on the other hand provides for a quantitative understanding of the whole complex of peculiar mechanical properties of crystals as will be shown by the author in a forthcoming publication in *The Physical Review*.

This theory also gives a satisfactory answer to the question why crystals exist at all and accounts for the heat of fusion, for the sharpness of the melting point and for cooperative volume effects in crystals. The postulate of the secondary structure therefore can be regarded as a more satisfactory working hypothesis than the conception of imperfections in crystals.

Smekal in his paper quotes the criticism which E. Orowan² recently published against the theory of the secondary structure. E. Orowan claims to have made more accurate calculations than the author. This accuracy, however, is obtained at the price of deliberately disregarding some very essential effects which I have introduced into my calculations and which cannot be omitted. Mr. Orowan's criticism consequently is based on entirely impossible premises. For details I must refer the reader to my related article on the physics of real crystals appearing in the *Helvetica Physica Acta*.

The particular problem of the influence of water on the plasticity of rocksalt which Smekal discusses can be satisfactorily treated only after the plastic properties of pure NaCl crystals have been quantitatively understood. As A. Smekal has not advanced any such theory his discussion is necessarily premature and unfounded.

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¹ A. Smekal, *Phys. Rev.* **43**, 366 (1933).

² E. Orowan, *Zeits. f. Physik* **79**, 573 (1932).

Band Spectrum of CS

Martin¹ obtained a spectrum attributed to CS in the region $\lambda 2418$ to $\lambda 2854$. We have photographed this band spectrum from a number of discharge tubes at both high and low dispersion, with the result that a total of some 170 heads, about one hundred of them new, have been recorded, extending from $\lambda 2400$ to $\lambda 3330$. The new bands fall into the vibrational array given by Jevons² extending the vibrational quantum numbers to $v' = 11$ and $v'' = 16$.

The strongest of the CS bands have been successfully photographed in the third order of a 21-ft. grating (dispersion of 0.66A per mm), the Q and P branches being clearly resolved to the origin. The majority of the bands have single P , Q , R branches, and are hence due to (${}^1\Pi \rightarrow {}^1\Sigma$) or (${}^1\Sigma \rightarrow {}^1\Pi$) transitions, as inferred by Jevons. Provisional

values for the moments of inertia are $I' = 37.3 \times 10^{-40}$ and $I'' = 35.1 \times 10^{-40}$ gram cm^2 , a difference of about 6 percent. This is in good agreement with the results for the band system of AIO. Results of this analysis will be reported at a future date.

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¹ Martin, *Proc. Roy. Soc.* **A89**, 127 (1913).

² Jevons, *Proc. Roy. Soc.* **A117**, 251 (1928).

Lack of Observed Hyperfine Structure in Strontium

Strontium has been stated by Aston to have three isotopes of mass 88, 86, and 87 of abundance respectively 83.3, 10, and 6.6 percent. Isotope 87 might be expected to show spin hyperfine structure. It is also possible that such structure could arise from isotopes 88 and 86 and structure because of isotopic displacements might be found in the strontium spectrum. The resonance lines of Sr II, $\lambda 4215.5$ ($5 {}^2S_{1/2} - 5 {}^2P_{1/2}$) and $\lambda 4077.7$ ($5 {}^2S_{1/2} - 5 {}^2P_{3/2}$)

were examined by Frisch¹ in the fourth order of 21 ft. grating and reported sharp, with a half-width in the case of $\lambda 4077$ of 0.20 cm^{-1} . Murakawa² in a paper on the h.f.s. of barium reproduces a plate of $\lambda 4215$ made with 1 cm Lummer-Gehrcke plate which seems to show a strong central component with an unresolved fainter component on either side. The description states that "the doublet separation of Sr⁸⁷ is about 0.140 cm^{-1} ." This is not neces-