

Note on a Relation between the Atomic Arrangement in Certain Compounds, Groups and Molecules and the Number of Valence Electrons

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The atomic arrangement in compounds and groups $(A_mX_n)^{-p}$ for which $v = n \times 8 + m \times 2$ is discussed, v being the total number of valence electrons per stoichiometric molecule or group. Available experimental data show that in such groups or compounds the atom A is usually displaced away from the center of the polyhedron formed by the surrounding atoms X . Simple rules for the amount of displacement are given. The interpretation of the observations in terms of the ionic theory and the theory of electron pair bonds is discussed.

IN THE following paper the crystal lattice of germano sulphide is described. GeS belongs to a large class of compounds, groups or molecules of the general formula $(A_mX_n)^{-p}$ which are characterized by the following features: None of the atoms A or X are transition elements. The total number of valence electrons per stoichiometric molecule or group, v , satisfies the condition $v = n \times 8 + m \times 2$, or if atom X is a hydrogen atom, $v = n \times 2 + m \times 2$.

On previous occasions I have had the opportunity to examine the atomic arrangement in several compounds or groups of this type.^{1,2,3,4,5} In one important respect the results of these investigations were of exceptional interest. Usually in crystal lattices it is found that an atom is situated at the center of the polyhedron formed by the surrounding atoms. However, it was found in many cases, where the condition $v = n \times 8 + m \times 2$ was satisfied, that the atom A was displaced away from the center of the polyhedron formed by the surrounding atoms X . Some examples may illustrate this statement: The groups $(SO_3)^{-2}$, $(ClO_3)^{-1}$, $(BrO_3)^{-1}$ have a pyramidal structure rather than the coplanar one found for $(NO_3)^{-1}$, $(CO_3)^{-2}$ and $(BO_3)^{-3}$.⁴ The $(NO_2)^{-1}$ group has been found to be angular rather than collinear like CO_2 .⁶ And now in GeS we will see that Ge is not lying at the center of the sulphur octahedra, as does Mg in MgS.

However, there are definite exceptions. Tl in $TlCl$, $TlBr$, TlI ⁷ is not displaced away from the center of the cubes formed by the surrounding halogen atoms. The analogous thing is true for Pb in PbF_2 , PbS , $PbSe$,

¹ W. H. Zachariasen, *Norske Vid. Akad. Skr. Oslo* **4**, 90 and 136 (1928).

² W. H. Zachariasen, *Zeits. f. Krist.* **71**, 501, 517 (1929).

³ W. H. Zachariasen, *Phys. Rev.* **37**, 775 (1931).

⁴ W. H. Zachariasen, *Jour. Amer. Chem. Soc.* **53**, 2123 (1931).

⁵ W. H. Zachariasen and H. E. Buckley, *Phys. Rev.* **37**, 1295 (1931).

⁶ G. E. Ziegler, *Phys. Rev.* **38**, 1040 (1931).

⁷ P. P. Ewald and C. Hermann: *Strukturbericht*, 1913-1928, Leipzig, 1931.

PbTe, PbI₂,⁷ for Bi in BiF₃ and BiI₃,⁸ for Sn in SnTe,⁷ and probably it is also true for Te in TeO₂⁷ and for I in the alkaliiodates.^{7,9} It is worth noticing, however, that the atomic number of atom *A* in all these cases is very high.

The empirical results we may formulate in a series of very simple rules:

In compounds or groups (A_mX_n)^{-p} satisfying the condition: $v = 8 \times n + 2 \times m$ (or if the atom *X* is hydrogen, the condition: $v = 2 \times n + 2 \times m$) the atom *A* is displaced away from the center of the polyhedron formed by the surrounding atoms *X*.

The amount of displacement decreases: (1) With increasing principal quantum number of atom *A*; (2) With an increasing number of valence electrons on the neutral atom *A*; (3) With increasing principal quantum number of atom *X*; (4) and probably with a decreasing number of valence electrons on the neutral atom *X*.

The absence of any displacement in crystals like SnTe, PbTe, TlI may thus follow directly from rule 1 and 3.

By expressing the rules in terms of the number of valence electrons and principal quantum numbers we have deliberately avoided any interpretation on the basis of existing theories for the chemical binding.

If we choose to take the standpoint of ionic bindings in the compounds or groups which we have considered, we would have to explain our rules as being due to a polarization of the ions *A*. As a matter of fact the empirical rules we have given would be a direct consequence of the ionic interpretation. We cannot therefore draw the conclusion that the bonds are truly ionic in character. It illustrates, however, the value of the ionic theory as a working hypothesis. As a matter of fact I have been able to predict correctly the atomic arrangement in a number of groups on that basis.¹

The rival to the ionic theory is, of course, the theory of the electron pair bond. It has been shown by Pauling¹⁰ and by Slater¹¹ that the structure of many of the groups which we have dealt with here can be satisfactorily interpreted in terms of electron pair bonds. As a matter of fact this interpretation offers in many cases distinct advantages compared to the ionic interpretation. However, this is no proof of the existence of electron pair bonds. It seems to me that serious modifications of the ideas of Slater and Pauling are necessary in order to account for all our observations. In GeS we found that Ge formed six bonds with sulphur atoms, three corresponding to an interatomic distance 2.58Å and the three others corresponding to 2.97Å. In the isomorphous SnS the difference between the two distances undoubtedly is smaller than in GeS, and then finally in PbS (having the ideal NaCl structure) we have six equivalent bonds. A comparison between the interatomic distances in As₄O₆ and Sb₄O₆ also shows this gradual transition towards six equivalent bonds as we pass towards higher atomic numbers (compare rule 1). Three of the bonds in GeS, As₄O₆ and Sb₄O₆ may, of course, be in-

⁸ H. Braekken, Zeits. f. Krist. **74**, 67 (1930).

⁹ W. H. Zachariasen and F. A. Barta, Phys. Rev. **37**, 1626 (1931).

¹⁰ L. Pauling, Jour. Amer. Chem. Soc. **53**, 1367 (1931).

¹¹ J. C. Slater, Phys. Rev. **37**, 481 and **38**, 325 (1931).

terpreted as electron pair bonds; but this interpretation is hardly satisfactory or justifiable in PbS for example.

It seems that the ideas of the electron pair bonds are fairly applicable in many cases for relatively low atomic numbers but of little use, in the present form at any rate, for high atomic numbers. In the lattices of As, Sb, Bi⁷ each atom is surrounded by six other atoms, three at a distance d_1 and three at a distance d_2 . The observed values of d_1 and d_2 are:

	d_1	d_2	α
As	2.51	3.15	97°
Sb	2.87	3.37	96°
Bi	3.10	3.47	94°

α is the angle between the three bonds corresponding to the distance d_1 . Pauling in his paper states that the approach of the bond angle towards 90° in this series indicates the transition to electron pair bonds formed by pure p eigenfunctions. This statement seems to me to be somewhat misleading. If namely the bond angle is exactly 90°, there will be six equivalent bonds, instead of two sets of three bonds. Other eigenfunctions than those of s and p electrons would have to be involved in the formation of six equivalent bonds.