

THE CHEMICAL BOND IN CRYSTALS WITH AN ANTIFLUORITE STRUCTURE
AND THE VALENCE POSSIBILITIES OF NEGATIVE IONS

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In connection with the problem of the high coordination numbers of anions in crystals consideration is given to the possibility of d-orbital utilization by negative ions.

1. Antifluorite type crystals of A_2IB^{VI} (Li_2O , Li_2S , Li_2Se , Li_2Te , Na_2O , Na_2S , Na_2Se , etc.) are usually considered as pure ionic compounds, $A_2^+B^{2-}$, with doubly charged anions. However, as was treated adequately in [1,2], there are grounds for believing that the effective charge on an anion cannot be much greater than unity. This follows from the fact that free, singly charged B^- ions show no affinity for a second electron and the lattice potential by itself can obviously not give rise to a new, bound state in a potential. Consequently, the formula of antifluorite type compounds should be more correctly written as $A_2^{\sim 0.5^+}B^{\sim 1^-}$, which is supported by the results of an x-ray determination of the effective charge on the "electronegative" atom (from the shift in the $K\alpha_{1,2}$ doublet; cf. the table which was taken from [3]). Thus the bond in the A_2IB^{VI} compounds has a significant degree of covalent character. One can obtain a graphical description of the character of this bond by considering localized, one-electron orbitals obtained by a unitary transformation of the "blokhovskikh" wave functions instead of the true one-electron functions ("blokhovskikh" waves of the valence zone). As Koster showed [4], such localized orbitals must be sought for each lattice point by solving the variation problem

$$\langle \varphi | \hat{H} | \varphi \rangle = \min \quad (1)$$

with the additional constraint that function φ be localized:

$$\langle \varphi(\mathbf{r}) | \varphi(g\mathbf{r}) \rangle = 0 \quad (2)$$

(g is an element of the space group of the crystal).

Obviously, the localized orbitals mentioned can be approximated at each B lattice point by an expansion over the basis of the orbitals of atom B and the A atoms that are in its first coordination sphere [2]. The tetrahedral environment of each A atom naturally indicates the participation of tetrahedral sp^3 functions of these atoms, $\chi_A^{(i)}$, $i = 1, 2, 3, 4$, in the localized orbitals. These are directed along the body diagonals of cubes with B atoms at the center and A atoms at the vertices (Fig. 1). The solution of the variation problem, (1), then leads to the calculation at each B lattice point of four linear combinations (the number of valence electrons per formula unit, A_2B , is 8) from 8 tetrahedral orbits, $\chi_A^{(i)}$, and from the atomic functions of the B atom, which we will take the s-, p-, and d-orbitals. It is logical to suppose that the four solutions corresponding to the lowest energy will be four degenerate orbitals of the type

$$\varphi_B^{(i)} = \frac{1}{\sqrt{1 + \lambda^2}} \left\{ \chi_B^{(i)} + \lambda \left(\frac{\chi_{A1}^{(i)} - \chi_{A2}^{(i)}}{\sqrt{2}} \right) \right\}, \quad (3)$$

where $\chi_B^{(i)}$ is the linear combination of B atom orbitals which gives maximum overlap with the corresponding $\chi_A^{(i)}$ orbitals. It is easy to show that such a combination will be four sd^3 hybrid orbitals of atom B. Thus, if

$$\chi_{A1}^{(i)} = \frac{1}{2} \{ s^A + p_x^A + p_y^A + p_z^A \}, \quad (4)$$

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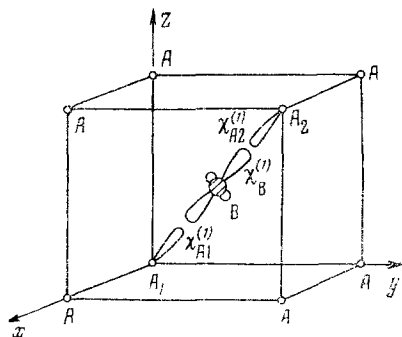


Fig. 1

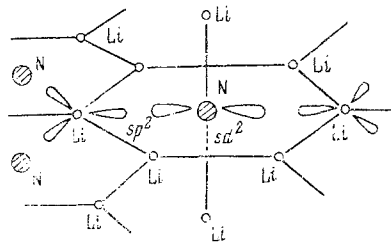


Fig. 2

$$\chi_B^{(i)} = \frac{1}{\sqrt{6}} s^B + \sqrt{\frac{5}{18}} \{d_{xy}^B + d_{xz}^B + d_{yz}^B\}. \quad (5)$$

In this way, for each A_2B formula unit there are four three-center orbitals of type (3) localized along four diagonals of a cube. They are completely filled with eight valence electrons from two A atoms and one B atom. Obviously all $4N$ of these orbitals (N is the number of formula units in the macrocrystal) can be considered to be mutually orthogonal so that the condition for localization, (2), is also satisfied.

2. It must be emphasized that such an interpretation of the chemical bonding involved in the cubic coordination about the B atom in anti-fluorite type crystals requires, of necessity, that the d-functions of the anion be used. Certainly in the case of compounds of S such utilization appears natural, and even more so in the case of Se and Te. At first glance it appears that this cannot be said of oxygen compounds such as Li_2O or Na_2O because the energy required to excite an electron to the 3d level of an O atom is very large (the energy of the low term, $5D \approx 97500 \text{ cm}^{-1}$ [5]) and would not be offset by an increase in the A—O bond stability. The situation changes, however, if we take into account the fact that O (as well as S, Se, and Te) is not present in the lattice in the form of neutral atoms, but as ions with a charge close to unity. The affinity of a neutral O atom for one electron, i.e., the ionization potential of the singly charged ion O, is a total of $1.47 \text{ ev} \approx 34 \text{ kcal/mole}$ [6] and the energy required to excite an electron to the 3d level of this ion must be of the same order. With such a small excitation energy it becomes likely that the utilization of d-orbitals in bonding is quite feasible. One might note that there is a maximum difference of about 17 kcal/mole between the electron affinities of S, Se, and Te atoms and the oxygen affinity ($F^S = 2.07 \text{ ev}$ [7], $F^{Se} = 1.7 \text{ ev}$, $F^{Te} = 2.2 \text{ ev}$ [8]). Consequently, the singly charged oxygen ion must resemble these atoms to a significant degree in its bonding capabilities. One must also say, however, that the problem of the valence capabilities of negative ions with a charge close to unity is quite vague because very small values of the ionization potential make practicable the excitation of electrons to still higher levels. Consequently, in considering only the 3d-functions we are limiting ourselves to the minimum basis needed to explain the stereochemistry. It is probable that the same description of the electronic structure can be applied to crystals in the $A_2^{II}B^{IV}$ series (Be_2C , Mg_2Si , Mg_2Ge , Mg_2Sn , etc.) which also belong to the antifluorite class. It is true that in this case it is hardly possible that one can take the charge on the B atom to be the same as in the isostructural $A_2^{IB}VI$ compounds. X-ray data [3] (see the table) show that this charge has a value of about 0.6. It should be pointed out, however, that even for this charge the energy needed to separate an electron from atom B is strongly diminished compared with the first ionization potential of the neutral atom and must be about 5 ev for C, about 4 ev for Si and Ge, and about 3 ev for Sn, so that the excitation energy to the 3d-orbital for the $C^{0.6-}$ atom, for example, is probably in the order of $\leq 5 \text{ ev}$. In view of the fact that in the usual transition from the s^2p^2 configuration to the sp^3 configuration for C the lowest term, 5S , is about 34000 cm^{-1} [5], this last value does not seem excessively high; even less so if we consider the lowering of the bonding triplet d_e in the cubic field surrounding the positive ions.

3. A similar use of d-orbitals can explain the cubic coordination about the metal atoms in $A^{II}B_2^{VII}$ compounds with a fluorite structure (CaF_2 , SrF_2 , BaF_2). The only difference from $A_2^{IB}VI$ and $A_2^{II}B^{IV}$ compounds is that the number of valence electrons per A_2B formula unit is sixteen in this case, not eight. Consequently, in addition to the four lowest energy solutions to the variational problem (1)

$$\varphi_{A,\text{bond}}^{(i)} = \frac{1}{\sqrt{1 + \lambda^2}} \left\{ \chi_A^{(i)} + \lambda \left(\frac{\chi_{B1}^{(i)} + \chi_{B2}^{(i)}}{\sqrt{2}} \right) \right\} \quad (6)$$

we must add four, higher energy "non-bonding" combinations

$$\varphi_{A,\text{non-bond}}^{(i)} = \frac{1}{\sqrt{2}} \{ \chi_{B1}^{(i)} - \chi_{B2}^{(i)} \} \quad (7)$$

	Compound	Charge on atom A	Charge on atom B
A_2B^{VI}	Na_2S	+0,75	-0,96
	K_2S		-1,06
A_2B^{IV}	Mg_2Si	+0,28	
	Mg_2Sn	+0,28	

for the case of $A^{II}B_2^{VII}$ crystals. Here, χ_B is an sp^3 -orbital of the B atom and χ_A is an sd^3 -orbital of the A atom. The possibility of such a utilization of d-orbitals from the metal atom is not contradicted by the experimental facts. For example, the excitation energy to a 3d-orbital of a neutral Ca atom amounts to about 20000 cm^{-1} , and for a positively charged ion, Ca^+ , only 13000 cm^{-1} [5]. One may add that the participation of d-orbitals in bonding is generally characteristic of the alkaline earth metals (other than Be and Mg). This is revealed, for example, in the experimentally observed deviation of the structure of the dihalide molecules from the linear [9].

4. The fluorite and antiferrofluorite structures discussed above are extremely interesting in two respects. First of all, fluorite-antiferrofluorite structures are interesting as examples of structures in which the chemical bond can be described (in relation to the "collective" properties in Dewar's terminology [11]) in the language of localized, one-electron functions and three-center orbitals. In compounds of this type these are less artificial than in the MgO -type lattice [2]. In the second place, one must emphasize the possibility that negative ions may use high-lying atomic orbitals and that, to a certain extent, this brings together the valence capabilities of the heavy and light elements. Similar utilization may be encountered rather frequently. It is probable, for example, that this occurs in Li_3N -type structures [10]. In this structure the Li atoms form a layer consisting of hexagonal rings with an N atom at the center of each ring. Krebs [12] explained the coordination about the N atom by resonance between two structures, in each of which three nitrogen sp^2 hybrid orbitals alternately were directed towards the vertices of the two triangles into which the hexagonal ring could be divided. Here, however, as in the case of the fluorite-antiferrofluorite structure, a description in the language of localized one-electron functions (also three-center) is more acceptable. In this description linear combinations are formed with sd^2 hybrid orbitals of the N atoms and sp^2 orbitals of the Li atoms (Fig. 2).

The utilization of high-lying d-orbitals probably occurs not only in crystals (where the role of the lattice may result in a significant stabilization of large effective charges) but also in isolated molecules. The hexacoordination of S in SF_6 is usually interpreted as the result of sp^3d^2 -hybridization of the sulfur orbitals [13]. Nevertheless, legitimate doubts have been expressed [14] concerning the possibility of this hybridization in view of the enormous excitation energy of the corresponding valence state. One must bear in mind, however, that this conclusion holds only for the neutral S atom. Actually, the S atom in SF_6 probably has a negative charge [16] because of the formation of donor-acceptor bonds involving its empty d_{xy} , d_{xz} , and d_{yz} -orbitals and unshared pairs of electrons from the F atoms [13]. The resulting negative charge on the S atom could lower the excitation energy of the valence state using d_z^2 - and $d_{x^2-y^2}$ -orbitals. It is possible that still another example of the use of d-orbitals is the hexacoordination of the C atom in the tetramer $Pt_4(CH_3)_{16}$.

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