

New Ways to Look at Solids

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Molecular organic and inorganic chemists frequently rely heavily on a variety of modern theoretical ideas in the areas of structure and reactivity. It often then comes as a surprise to find that in the domain of crystal chemistry, most structural theoretic ideas are, by comparison, rather old-fashioned and often naive. In this account we will initially explore some of the reasons for this state of affairs and then illustrate some new directions which appear to be promising ones for solids. Some of them rely heavily on modern molecular ideas, but one tackles a problem largely ignored by molecular inorganic chemists.

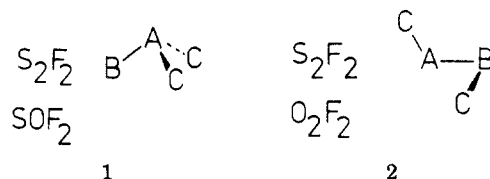
The past decade or two has seen a considerable leap in the level of our understanding of the electronic structures of small molecules. Substantial progress has been made in the area of fast and accurate numerical solutions of the Schrödinger wave equation, but probably the most important global advances have been associated with rather simple approaches based on symmetry and overlap, underwritten by rather crude semiempirical calculations. Witness the success of the Woodward-Hoffmann rules, initiated after the development of the extended Hückel method in the early sixties. Today the general features of the geometries of inorganic molecules, namely approximate bond angles, relative bond lengths of symmetry inequivalent linkages, and ligand site preferences, are now really quite well understood by using a variety of simple theoretical approaches based on one-electron molecular orbital theory.¹ Frontier molecular orbital ideas are now extensively used by organic chemists to guide synthetic strategy, and the isolobality principle has sewn together many kinetic and structural aspects of organic and inorganic chemistry through studies on organometallic compounds.^{2,3}

By way of contrast, there is very poor understanding concerning the electronic factors which comprise the numerology of chemistry, namely bond dissociation energies, heats of formation, and the energetics associated with molecular reaction pathways. Even reliable numerical calculation of such properties by high quality methods is at present beyond our reach for systems of any complexity.

Such haziness extends to what we will call the coordination number problem, associated with linkage isomers. For example we do not really *understand* the factors determining the geometries of ABC₂ systems (1 or 2) in the same way we understand those influencing angular geometries.

We may compare this thumbnail sketch of the molecular scene to one of the solid state.⁴ There are

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virtually no electronic theories of structure and bonding of the type we have described for molecules outside the traditionally based Pearson and Grimm-Sommerfeld valence rules.⁵ The reason for this rather striking difference is twofold. First the description of solid-state structures, in the sense of how one arrangement is related to another, and the systematic enumeration of all geometrical possibilities for each stoichiometry is an extremely complex task even for simple systems. The techniques of combinatorial analysis⁶ help out a lot for small subsets of this problem, as we shall mention later, but the global structural classification problem is still largely unsolved. It is therefore difficult at present to generate all the likely geometrical candidates for a particular stoichiometry. There are frequent experimental surprises as illustrated by a recent Account⁷ even for "simple" systems.

Secondly, whereas molecular chemists are more interested in the nuances of angular geometry possibilities, solid-state chemists are more prone to ask why one particular structure is favored over another which is topologically different. For example, the AB octets fall into six structural types (CsCl, NaCl, ZnS, ZnO, red PbO, and graphite) that contain four different coordination numbers. This is just the area where simple theory is most deficient and has resulted in very slow progress in understanding solid-state structure. We will show in this Account a few ways in which these problems may be tackled by building on ideas which have been profitable ones for molecules.

"Molecular" Methods in the Solid State

We first use an approach which has been pedagogically useful for molecules. The details of a particular structure are best viewed by comparison with those of electronically or structurally related systems. It is instructive, for example, to contrast the planar structure of BF₃ (24 electrons) with pyramidal NF₃ with two more electrons. The response of a parent structure to the presence of extra electrons, which here would occupy high-lying orbitals, may not only result in different angular geometries but can lead to increasingly broken up structures. Both processes result in stabilization of

(1) Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980.

(2) Hoffmann, R. *Science (Washington, D.C.)* 1981, 211, 995.

(3) Mingos, D. M. P. *Adv. Organomet. Chem.* 1977, 15, 1.

(4) O'Keeffe, M.; Navrotsky, A. "Structure and Bonding in Crystals"; Academic Press: New York, 1981.

(5) (a) Pearson, W. B. "Crystal Chemistry and Physics of Metals and Alloys"; Wiley: New York, 1972. (b) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: New York, 1974.

(6) McLarnan, T. J.; Moore, P. B., in ref 4.

(7) Corbett, J. D., *Acc. Chem. Res.* 1981, 14, 239.

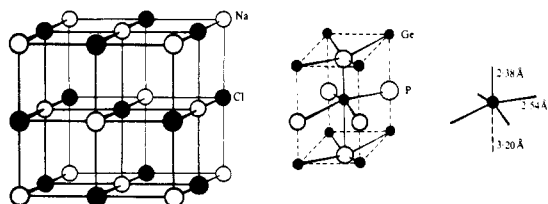


Figure 1. Distortion of the eight-electron rocksalt structure to that of GeP (high pressure form).

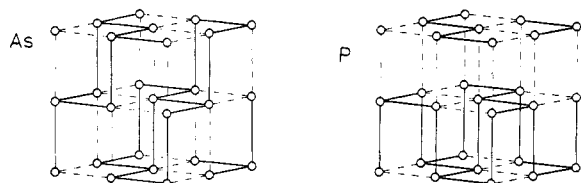


Figure 2. Two bond-breaking possibilities of the rocksalt structure which give universal trigonal pyramidal coordination: (a) GeTe or arsenic structure; (b) GeS or black phosphorus structure.

the distorted geometry as these high-lying occupied antibonding orbitals become lone pair orbitals of lower energy. Chart I shows the response of the 20-electron P_4 or tetrahedrane structure to the presence of extra skeletal electrons. Note that when more than one bond is broken linkage isomers become possible, and in this case, we face the coordination number problem noted above. Such ideas are also of use in solids,⁸ and may be used for a variety of structural types.

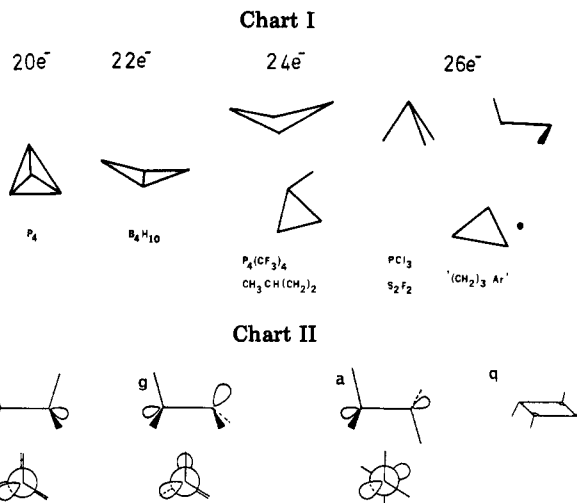
One example, depicted in Figure 1, shows the rocksalt structure (stable for eight electrons per AB unit in the absence of d orbitals and lone pairs) and how it is distorted in the nine-electron species GeP. Each atom, octahedrally coordinated in rocksalt, is now in a square-pyramidal environment. With two extra electrons (Figure 2) the structures of GeS (a derivative⁹ of black phosphorus) and GeTe (a derivative⁹ of arsenic) may be reached¹⁰ by breaking three mutually perpendicular linkages around each center to give a lone pair and trigonal-pyramidal coordination.

We now pose the questions which will lead to the solution of a subset (albeit a small one) of this general structural problem. (i) How many different ways are there of breaking up the rocksalt structure in this way to give universal trigonal-pyramidal coordination? (ii) Of these possible structures, how many are actually observed experimentally? (iii) What are the electronic factors which determine the stability of these structures? The first of these is a nontrivial problem but one which can be solved by the use of modern combinatorial techniques.¹⁰ For a rocksalt-sized unit cell a total of 36 possibilities only exist and, of these, we have already mentioned GeS (black phosphorus) and GeTe (arsenic) layer structures, which are well-known. To these we can add two framework structures, those of α - $Hg_3S_2Cl_2$ and $La_2Be_2O_5$, which may be derived from rocksalt in a similar way.^{5b} To answer the third question, we need to look at some calculations, but note that since all these species contain three-coordinate atoms

(8) Burdett, J. K. *Nature (London)* 1979, 279, 121.

(9) A derivative structure is one where the overall topology of the parent arrangement is maintained but some of the atoms have been replaced by others. Here half of the atoms of black phosphorus or arsenic have been replaced by Ge and the other half by chalcogen.

(10) Burdett, J. K.; McLarnan, T. J. *J. Chem. Phys.* 1981, 75, 5764.



the coordination number problem is avoided here (i.e., we do not compare these ten-electron structures with, for example, the red PbO arrangement which contains four coordinate atoms).

Complications immediately arise. Such solids are molecules of infinite extent with a correspondingly infinite number of "molecular orbitals". However, for a crystalline solid there are well-known ways around this problem.¹¹ We shall not discuss the operational details involved but simply say that, just as in the molecular area, there are a range of techniques available of varying degrees of sophistication.¹² Numerically we find¹³ the very satisfying result that the black phosphorus structure is calculated to be lowest in energy of the 36 possibilities, arsenic is seventh lowest, and the two observed framework structures are third and fourth.

However it is vital to correlate these results, produced after a considerable amount of number crunching, with well-known molecular concepts. Each atom is trigonally pyramidally coordinated, so the reasons for the energetic differences between structures must lie at the second nearest-neighbor level or perhaps even further away. Each structure may be geometrically characterized by a set of indices (s , a , g , q) which describe the number of syn, anti, gauche, and quadrilateral arrangements in each unit cell; see Chart II. Using this observation we find the rather dramatic result that eq 1 fits¹³ the band structure energies extremely well, with values of $E_s = -56.787$ eV, $E_g = -57.036$ eV, $E_g = -57.071$ eV, and $E_q = 0.994$ eV. E_q is a destabilizing

$$E_T = sE_s + aE_a + gE_g + qE_q \quad (1)$$

energetic contribution compatible with our current views of the stability of such arrangements in organic compounds. E_s is the least stable of the second-nearest-neighbor geometries, as might be expected from VSEPR arguments. What is perhaps surprising is that E_g and E_t are close in energy. However, from molecular chemistry we know that in molecules isoelectronic with fragments of these structures (N_2F_4 , O_2H_2 , P_2F_4 , N_2H_4 , etc.) the "gauche effect" is extremely important¹⁴ and

(11) For example: Harrison, W. "Electronic Structure and Properties of Solids"; Freeman: San Francisco, 1980.

(12) We have used a band structure program employing the extended Hückel method, written by M.-H. Whangbo, to whom we are grateful.

(13) Burdett, J. K.; Haaland, P.; McLarnan, T. J. *J. Chem. Phys.* 1981, 75, 5774.

(14) Wolfe, S. *Acc. Chem. Res.* 1972, 5, 102.

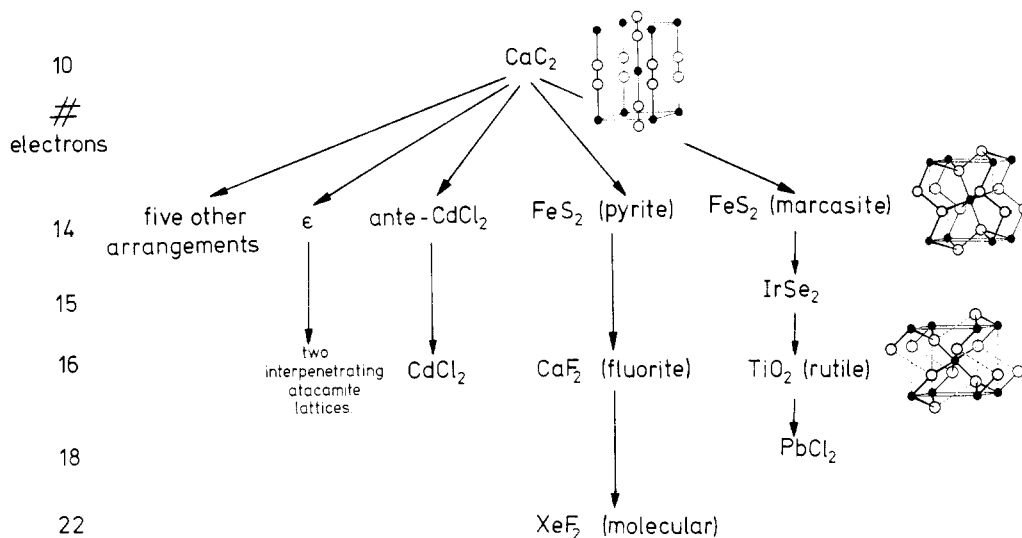
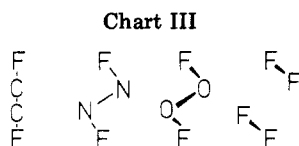


Figure 3. Response of the ten-electron CaC_2 structure to the presence of additional electrons. Shown pictorially as an example are the structures of one sequence via marcasite to rutile and PbCl_2 . In IrSe_2 one-half of the X-X linkages are broken. There is no example of the "ante-cadmium halide" type (cadmium halide with X-X links between adjacent layers), but with interlayer spacers the structures of NaHF_2 and the delafossite $\text{M}^{\text{I}}\text{M}^{\text{III}}\text{O}_2$ structure are found.



that gauche and trans geometries are often close in energy. The theoretical reasons for this effect in molecules are known and immediately lead us to an understanding of the stabilities of the related solid state structures.

Figure 3 shows another series which can be viewed¹⁵ along similar lines. The CaC_2 structure is found for several systems with ten electrons per AX_2 unit. With additional electrons, first the X_2 units tilt to give the pyrite and marcasite arrangements and related structures. There are, in fact, nine possible structures of this type, but three are calculated to lie lower in energy than the other six; they are the ones where lone pair-lone pair repulsions between X_2^{2-} units are minimized. These are the ones which are observed. With more electrons the X_2 units split apart to give the classic 16-electron structures containing isolated X atoms. There is an immediate resemblance to similar behavior in A_2X_2 molecules as the number of electrons increases; see Chart III. Eventually we can very simply generate the molecular solid formed by XeF_2 by breaking six of the eight A-X linkages of the fluorite structure. These structural/electronic ties are invaluable in bringing together structures, seemingly unrelated at first sight.

Another approach which may have great promise in crystal chemistry is use of the fragment formalism. One way to understand the orbital pattern of complex molecules is to assemble the structure from fragments with readily understood orbital properties. This fragment approach, via the isolobal principle,¹⁻³ has been invaluable in understanding the electronic structures of inorganic and organometallic cage and cluster molecules.^{1,2} A similar technique may be used in the solid state¹⁶⁻¹⁸ and has been used to rationalize the occurrence

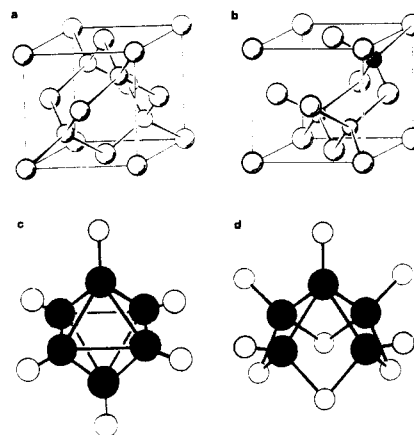


Figure 4. The structures of (a) cubic diamond, (b) CdIn_2Se_4 , (c) $\text{B}_6\text{H}_6^{2-}$, and (d) B_5H_9 .

of A-A, A-X, and X-X linkages in some tetrahedrally based AX structures as a function of electron configuration.

Fragments of almost all extended arrays in the solid state contain cages of atoms, many with shapes familiar to the molecular chemist. Note the strong resemblance, for example, between the cubic diamond structure of Figure 4a and that of adamantane ($\text{C}_{10}\text{H}_{16}$). We might ask whether there are any theoretical similarities too. A clue lies in the existence of stoichiometric ordered defect structures such as $\square\text{CdIn}_2\text{Se}_4$ where one atom of the diamond cage is missing (Figure 4b). We use the \square symbol to draw attention to this point in the chemical formula.

A simple relationship, the Grimm-Sommerfeld^{15a,19} valence rule, holds for almost all tetrahedrally based structures of this type. It simply requires an average of four valence electrons per site. If the chemical formula is written as $\prod N_n$ to indicate the presence of n atoms with N electrons (diamond is then written as 4_1 and $\square\text{CdIn}_2\text{Se}_4$ as $0_12_13_26_4$ where 0 = defect), then

$$\sum nN_n / \sum n = 4 \quad (2)$$

(15) Burdett, J. K.; McLarnan, T. J. *Inorg. Chem.*, in press.

(16) Burdett, J. K., in ref 4.

(17) Burdett, J. K.; Lin, J.-H. *Acta Cryst., Sect. B* 1981, 37, 2123.

(18) Burdett, J. K. *J. Am. Chem. Soc.* 1980, 102, 450.

(19) Parthé, E. "Crystal Chemistry of Tetrahedral Structures"; Gordon and Breach: New York, 1964.

Table I
Analysis of the Spinel Data Base in Terms of CFT

spinel type	no. of examples	no. without d-block elements	no. with only d^0 , d^5 , d^{10} ions	no. with no available data ^a	no. where CFT can predict ^b	no. of errors ^c
AB_2X_4						
$X = O; 6:1^d$	4	0	4	0	0	0
4:2	30	3	6	12	9	3
2:3	63	3	11	8	41	5
$X = S, Se, Te$	75	10	32	9	24	5
A_3X_4	4	0	0	0	4	0
$AB_2(CN)_4$	6	0	6	0	0	0
$AB_2(Hal)_4$	55	1	2	0	2	0
total	187	17	61	29	80	13

^a Required spectral data not available. ^b Assumes that for $X = S, Se, Te$ the relative magnitudes of the octahedral site preference energy is the same as for oxide spinels. ^c The best success rate achievable, obtained by assuming, for example, that $FeMn_2O_4$, $CrMn_2O_4$ and $MnCo_2O_4$ have electron distributions such that they are $Fe^{II}Mn^{II}Mn^{III}O_4$, $Cr^{III}Mn^{II}Mn^{III}O_4$, and $Mn^{III}Co^{II}Co^{III}O_4$ (an assumption in keeping with their relative ionization potentials). ^d These numbers refer to the formal oxidation states of A, B, e.g., a 2:3 spinel is $A^{II}B^{III}X_4$.

There are clearly many combinations of vacancies and atomic building blocks possible which fit this formula.^{1,19} The mineral nowakiite, for example, is $\square Cu_6Zn_3As_4S_{12}$ or $O_11.6235_46_{12}$. The similarities between this behavior and that controlling the shapes of boranes, carboranes, metallocarboranes, and metal cluster compounds are striking. Following the ideas of Wade²⁰ and Mingos,³ an m vertex deltahedron is stable for a total of $m + 1$ skeletal electron pairs²¹ or $2(m + 1)/m$ electrons per site. Just as in the solid-state examples of diamond and $CdIn_2Se_4$, we find structures with a complete complement of vertices which satisfy this requirement (for example, the closo-octahedral geometry of $B_6H_6^{-2}$ shown in Figure 4c), species with one missing vertex (for example, the nido-octahedral geometry of B_5H_9 shown in Figure 4d), and arachno species with two missing vertices, etc. Even at this rather superficial level, the similarities between the two sorts of system are very strong ones^{1,8} and suggest the application of similar theoretical ideas to both areas. Molecules and solids are not *all* that different after all.

An Approach to the Coordination Number Problem

The best known approach to this problem in solids is the use of Pauling's radius ratio rules, which predicts the most stable coordination number for A_mB_n compounds according to the ratio of the "billiard ball" radii of the two "ions". Although conceptually pleasing, this model is in fact very unsuccessful at predicting structures and is also unsatisfactory in that these "ionic radii", derived from the observed crystal structure, vary both with coordination number and the nature of the counterion. The approach is also not applicable to species which we might regard as largely covalent. Other approaches to the problem have used two structural indices to construct a two-dimensional display where every compound in the class under consideration is represented by a point. Thus Mooser-Pearson^{5a} diagrams use \bar{n} , the average valence principal quantum number of the atoms in the formula unit, and $\Delta\chi$, the AB Pauling electronegativity differences, as indices. If such a diagram can be divided into distinct regions containing all compounds of the same structure, using a "Mendeleev" approach to construct the best boundary lines,²²⁻²⁴ rather than the results of some

detailed theory, then for large databases, it is reasonable to assume that the two indices must represent factors which are important in structural determination. Such diagrams are good for octet AB systems, but for A_mB_n systems in general, they only sort coarsely by coordination number. Crystal ionic radii do, in fact, sort structures reasonably well^{25,26} when used as indices in this way (Figure 5), and it is only the imposition of the boundaries derived from a highly idealized mechanical model which has qualified the early ideas of Pauling in this regard. "Ionic" size appears to be important in determining solid-state structures but not in the radius ratio sense.

Recently, there has been considerable interest in a new class of structural maps which use combinations of pseudopotential radii (r_i) as structural indices and can lead to highly successful structural sorting diagrams for AB compounds.²²⁻²⁹ These radii are not model dependent in the sense that "ionic", "covalent", or "van der Waals" radii are. However the function $r_\sigma = r_s + r_p$, which we can use as a measure of atom "size", do scale²³ with crystal radii of different types, although the proportionality constant is dependent upon the row of the periodic table. Since the radii describe the potential experienced by the valence electrons, they are inversely related to the corresponding valence orbital ionization potentials. So the quantity $\chi = 1/r_s + 1/r_p$ is a good way to characterize the electronegativity of an atom in the Mulliken sense.

Both r_σ and χ make excellent indices with which to sort^{25,26} structures for both AB octets (not shown) and AB_2 double octets (Figure 5). Furthermore, the same indices, r_σ^A, r_σ^B (Figure 6) and χ^A, χ^B (not shown), can also structurally sort spinels into the normal $\{A\}[B_2]X_4$ and inverse $[A]\{B\}[B]X_4$ structures,²⁷ where $\{ \}$ represents tetrahedral, and $[\]$ octahedral, coordination in the cubic-close-packed $X =$ chalcogen lattice. There are only four obvious errors. This particular site preference

(22) Bloch, A. N.; Schatteman, G. C., in ref 4.

(23) Zunger, A., in ref 4.

(24) Phillips, J. C. *Comments Solid State Phys.* 1978, 9, 11.

(25) Burdett, J. K.; Price, G. D.; Price, S. L. *Solid State Commun.* 1981, 40, 923.

(26) Burdett, J. K.; Price, G. D.; Price, S. L. *Phys. Rev. B* 1981, 24, 2903.

(27) Burdett, J. K.; Price, G. D.; Price, S. L. *J. Am. Chem. Soc.* 1982, 104, 92.

(28) McClure, D. S. *Phys. Chem. Solids* 1957, 3, 311.

(29) Burdett, J. K.; Price, S. L. *Phys. Rev. B* 1981, 22, 5462.

(20) Wade, K. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1.

(21) $(m + 2)$ pairs for the tetrahedron.

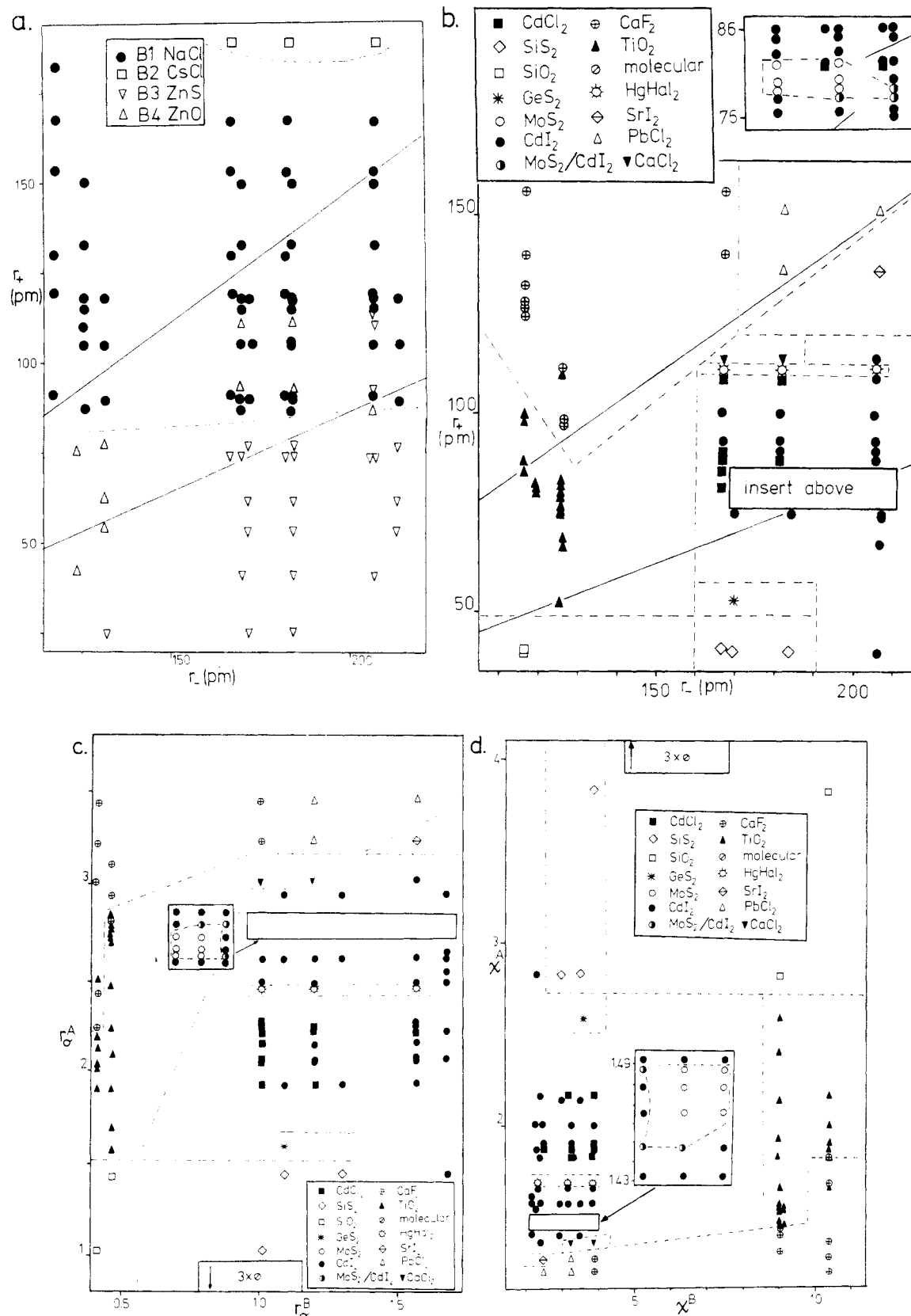


Figure 5. Structural sorting maps for (a) AB octet and (b) AB₂ double octet systems using Shannon and Prewitt radii as indices. The cation radius is often coordination number dependent, and we have chosen values commensurate with the observed structure. (Solid lines are those imposed by the radius ratio rules, dashed lines are drawn using a Mendeleev philosophy.) (c) and (d) show structural maps for AB₂ double octets using r_+ and χ as indices. The only apparent errors are the polymorphic ZrO₂ and the d⁸ system PdF₂. In these maps all points labeled with the same symbol represent examples of the same structure type. For example, LiF, CsF, RbCl, NaBr, etc. all crystallize in the NaCl structure type.

problem has been traditionally rationalized in terms of the purely d electron effects determining the relative

crystal-field stabilization energies. In fact, it is only successful in about three quarters of the examples

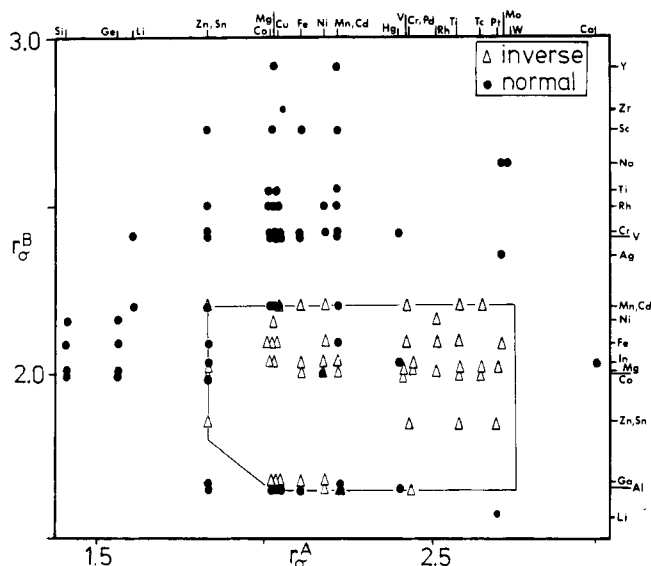


Figure 6. Structural sorting map for 172 spinels AB_2X_4 (where A, B are different and X = chalcogen). There are four errors (two points are coincident) but only for two of these is the experimental data unequivocal in assigning the site occupancy.

where the theory can make a prediction and the necessary spectral data are available (Table I). Crystal field arguments, do, however, explain the structures of the species located on the boundaries between the normal and inverse fields of Figure 6. This result suggests that the cation distribution is primarily determined by the atomic size or electronegativity (dominated here by s and p functions) and that crystal field effects are of secondary importance. This last comment, recognized by many early workers²⁸ in this field, has often been forgotten over the years.

Energetic information is also contained in the r_σ plots. For example, heats of reaction involving octets²⁹ and spinels³⁰ fit quite well with a simple function based on r_σ differences.

We may learn a good deal about the factors influencing coordination number and hidden within these structural maps by looking at the site preference problem in molecules.^{1,31} Within the one-electron approximation, the total electronic energy of a structure, with a given geometry and electron distribution, is given roughly by eq 3, in which H_{ii}^ξ is the Coulomb integral

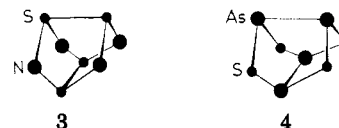
$$E = \sum_{i,\xi} q_i^\xi H_{ii}^\xi \quad (3)$$

for the i th orbital, located on the atom ξ , and q_i^ξ is the gross Mulliken charge associated with this orbital. In a closely related molecule, with the same electronic configuration but when some of the atoms are now different, the spirit of first-order perturbation theory suggests that the lowest energy structure will result from eq 3 when the atoms with the largest $-H_{ii}^\xi$'s (largest electronegativity in the Mulliken sense) occupy the sites with the largest q_i^ξ .

(30) Price, G. D.; Price, S. L.; Burdett, J. K. *Phys. Chem. Min.* (in press).

(31) See also the related problem in sulfuranes where this technique is used: Hoffmann, R.; Howell, J. M.; Muettterties, E. L. *J. Am. Chem. Soc.* 1976, 98, 2484.

We can use this result to view the coordination number problem in the isoelectronic pair of A_4X_4 molecules As_4S_4 and N_4S_4 . Both structures are based on an intermeshed square plane of X atoms and a distorted tetrahedron of A atoms (a gable disphenoid). The result is two-coordinate A and three-coordinate X atoms. Interestingly in As_4S_4 the sulfur atoms occupy the two-coordinate sites (3) and in S_4N_4 the three-coordinate sites (4). A calculation on a 44-electron X_8 unit



with this geometry shows that the two-coordinate sites carry the negative charge and therefore attract the more electronegative atoms, sulfur in As_4S_4 and nitrogen in S_4N_4 . This perhaps unusual structural result (nitrogen atoms are more often three-coordinate) is thus understandable. The general result, followed reasonably well by many compounds, is that the more electronegative atoms prefer the sites of lowest coordination number.

For the general coordination number problem, imagine a collection of possible structures, each with a set of charges $\{q_i^\xi\}$ which describe the "latent" s and p orbital charges for each inequivalent atom ξ for a given electronic configuration. The lowest energy structure will then be the one that maximizes the function of eq 3 via optimal matching of $\{q_i^\xi\}$ and $\{H_{ii}^\xi\}$. The actual form taken by the $\{q_i^\xi\}$ will, of course, depend on the numerical details of the calculation on the geometry. However, the $\{H_{ii}^\xi\}$ are set by the nature of the atoms themselves and are related, as we have mentioned, to the pseudopotential radii, r_i^ξ . This analysis then suggests that structural maps, via judicious choices of indices in terms of the r_i , sort structures because they mimic the charge control of coordination number.³²

To understand the exact location of the boundaries between different structures is, however, a much tougher problem and one which we leave for the future. It is interesting to note, however, that the electronegativity arguments which are used to understand site preferences in molecular chemistry also appear to play a major role in determining solid-state structures. Thus very strikingly in crystal chemistry, we are able to link together such modern electronic ideas (via ionization potentials and Mulliken electronegativities) and the traditional approach based on "size". These ideas, like those earlier in this Account, have hardly scratched the surface of this gigantic problem, but perhaps have given us a glimpse as to likely directions of progress for the future.

The chemistry described in this Account is the result of the interaction of a small group of people with diverse backgrounds, in particular, Peter Haaland, Jung-Hui Lin, Timothy J. McLarnan, Sarah L. Price, and Geoffrey D. Price. It was made possible by the stimulating environment at the University of Chicago and by generous funding from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

(32) Burdett, J. K.; Price, S. L. *J. Phys. Chem. Solids* (in press).