

Factors influencing solid-state structure—an analysis using pseudopotential radii structural maps

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(Received 4 May 1981)

Structural sorting maps using R_σ/R_π , r_+/r_- , r_σ^A/r_σ^B , and χ^A/χ^B are compared for AB , AB_2 octets and double octets, and AB_2X_4 spinels. With the use of r_+/r_- , the crystal ionic radii, the sorting is tolerable only if the usual restrictions of the mechanical model (radius ratio rules) are relaxed. R_σ/R_π are poor indices for AB_2 and AB_2X_4 , but r_σ^A/r_σ^B and χ^A/χ^B are excellent for all three systems. It is suggested that the traditional packing ideas based on size (and viewed semiquantitatively here using the $r_\sigma^{\frac{5}{6}}$) are directly related to modern charge-control aspects (via electronegativity differences) of molecular structures, and both can be viewed as very important factors in determining structural preference.

INTRODUCTION

As an alternative to the use of numerical quantum-mechanical calculations to investigate the relative stabilities of different solid-state structural alternatives, a “Mendeleevian” philosophy to study this problem has been increasingly popular in recent years.¹⁻⁹ Structural sorting maps of various types, constructed in such a spirit, have been very successful in producing a topological clustering of species with the same structure. These maps consist of two-dimensional displays where one carefully chosen index is plotted against another for a large compound data base. Several physical constructs have been used as indices ranging from Pauling electronegativities, ionicity, values of principal valence quantum numbers, and, more recently, combinations of pseudopotential orbital radii.

One of the reasons for following such an approach is the hope that it will eventually lead to a global *understanding* of why solids adopt the structures they do, via interpretation of the indices used in these two-dimensional displays. In this note we show that R_σ and R_π , used initially by St. John and Bloch² for AB octets, do not lead to good sorting for either the double octet AB_2 or AB_2X_4 spinel systems. We reevaluate the use of crystal radii as structural sorting indices and then show that two very simple indices, with intimate links to both traditional and contemporary ideas of molecular and solid-state structure, sort AB , AB_2 , and AB_2X_4 systems extremely well.

AB OCTETS

A time-honored example of a simple approach to this structural problem lies in Pauling's first rule,¹⁰ which links the coordination number of an ion with the ratio of its “radius” to the radius of the “ions” forming its coordination polyhedron. In terms of a mechanical model,¹¹ the rule predicts that the lines $r_+/r_- = (\sqrt{3}-1)$ and $r_+/r_- = (\sqrt{2}-1)$ will define the boundaries between eight and six coordination and between six and four coordination, respectively, on a two-dimensional display using the radii r_+ and r_- as indices.¹² Figure 1 shows such a plot for the AB octets. The major drawback with this, perhaps conceptually satisfying approach, is that it is just not successful (Table I). Another disadvantage is that the radii are derived from the AB distances in the crystal themselves, and often are strongly counter ion and coordination-number dependent. (We do note in this context the computation of first-principles pseudopotential-derived¹³ crystal radii.) Figure 1 takes this into account and uses the radii appropriate to the observed coordination number. Even so with a data base of 98 AB octets, for which ionic radii are available, 38 errors result. If, however, we remove the restrictions of the mechanical model, and follow a Mendeleevian philosophy in drawing the boundaries, using r_+ and r_- as structural indices, we can choose the location of the boundary lines to give a much better sorting (7 errors in 98). Interestingly there are no

dramatically misplaced examples but just a gray area between six and four coordinate structures which contain examples of both types.

Good structural sorting may also be achieved by using pseudopotential radii. In separate studies Bloch and co-workers,⁴ Phillips and Chelikowsky,⁷ and Zunger⁹ have produced very impressive sortings of AB octet compounds using combinations of pseudopotential atomic radii as structural indices. Defining $r_{\sigma}^{\xi} = r_s^{\xi} + r_p^{\xi}$ and $r_{\pi}^{\xi} = |r_p^{\xi} - r_s^{\xi}|$ then the indices R_{σ} and R_{π} are constructed as in Eqs. (1) and (2):

$$R_{\sigma} = |(r_s^A + r_p^A) - (r_s^B + r_p^B)| \\ = |r_{\sigma}^A - r_{\sigma}^B|, \quad (1)$$

$$R_{\pi} = |r_p^A - r_s^A| + |r_p^B - r_s^B| = r_{\pi}^A + r_{\pi}^B. \quad (2)$$

Here r_s , r_p are the crossing points of the nonlocal pseudopotential $V_{\text{eff}}^l(r)$. ($l = 0, 1, 2$ for s, p, d .) They may be obtained empirically via the atomic spectra of nontransition elements¹⁴ or by a first-principles route^{6,15} for both main-group and transition elements. The quality of the sorting achieved in these studies is such that R_{σ} and R_{π} must somehow reflect the major factors influencing structural preference. However, it should be remembered that, as in all such Mendeleevian approaches, no *a priori* predictions are made about the location of the boundary lines.

As we pointed out, if the crystal radii r_+ and r_- are used as indices for a structural sorting map, a tolerable sorting is achieved. It is only the imposition of the "billiard ball" boundaries which produce an unacceptable number of errors. Since the function r_{σ} , defined above, scales⁶ approximately with Pauling's tetrahedral radius, can r_{σ}^A and r_{σ}^B be used successfully as indices even through they describe a "core" rather than crystal radius? The answer is, yes, and Fig. 2 shows the resulting sorting map which contains only two errors, MgS and MgSe if the radii of Bloch and Schatteman⁴ are used. Both of these species have extremely small transition enthalpies to the sphalerite structure.⁶ By way of comparison, Zunger found three misplaced AB octets (using this data base) with R_{σ} and R_{π} as indices with his first-principles radii.⁶ Bloch and Schatteman⁴ using slightly differently defined indices and empirically computed radii report a perfect separation. If we use Zunger's radii and r_{σ}^A , r_{σ}^B the separation is poorer than that shown in Fig. 2. The problem appears to lie in the values of r_s and r_p for lithium, which leads to the incorrect location of several lithium compounds.

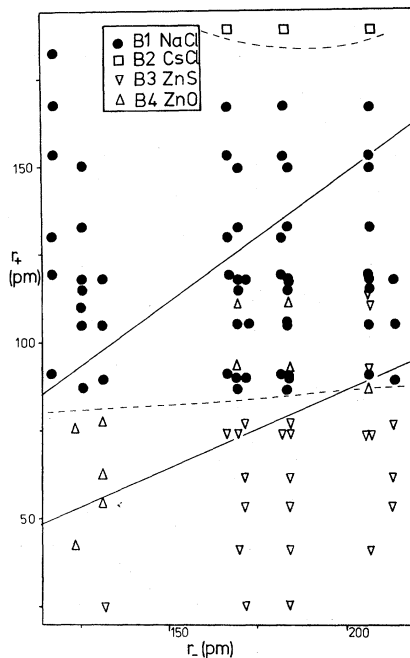


FIG. 1. Structural map for AB octet compounds using the crystal radii (Ref. 12) r_+ and r_- corresponding to the observed coordination geometry. The data base of 99 AB compounds was extracted from Ref. 6 and is listed in the Appendix. SiC cannot be plotted as the crystal radii are not available. The solid lines represent the radius ratio rule boundaries between the 8:8 (CsCl), 6:6 (NaCl), and 4:4 (zinc blende and wurtzite) coordination structures, the dashed lines are those which sort the data base best into 4, 6, and 8 coordination. The mechanical model should be a plot of $r_<$ and $r_>$, i.e., the larger and smaller of the two radii; in the present case CsF and KF are incorrectly located using r_+ and r_- , but are found in the correct area predicted by the mechanical model if $r_<$ and $r_>$ are used. (Sc,Y,La)Bi, with the NaCl structure lie off the right-hand side of the plot and are sorted correctly.

A slightly better sorting by coordination number is found (Fig. 3) if the functions

$$\chi^{\xi} = (r_s^{\xi})^{-1} + (r_p^{\xi})^{-1} \quad (3)$$

are used ($\xi = A, B$). Since the r_l scale inversely with the orbital ionization potential, this function is a quantitative measure of that rather ambiguous concept, electronegativity. [Weighted versions of Eq. (3) have also been used^{2,7,16} in the past.] In Fig. 3 there are also three errors, using Bloch and Schatteman's radii. Two compounds with the sphalerite structure appear in the wurtzite region. The two structures differ only at the third-nearest-

TABLE I. Failure rate for structural sorting maps.

	AB octets	AB_2 double octets	AB_2X_4 spinels ^c
r_+/r_-^a			
radius ratio	38/98	18/109	
Mendelejev	7/98	3/109	8/48
R_σ/R_π			
Zunger radii	3/108	$\sim 30/112^b$	$\sim 32/172$
Bloch and Schatteman radii	0/108		d
r_σ^A/r_σ^B			
Zunger radii	8/99	2/112	4/172
Bloch and Schatteman radii	2/99	1/61	d
χ^A/χ^B			
Zunger radii	7/99	1/112	4/172
Bloch and Schatteman radii	3/99	1/61	d

^aSorting by coordination number only.

^bSorting is so bad (Fig. 7) that this ratio has little comparative meaning.

^cUsing crystal-field theory, for the 74 examples where spectroscopic data is available, and for which a prediction can be made, there are 13 errors.

^dSince Bloch and Schatteman (Ref. 4) do not give radii for transition-metal atoms, their radii cannot be universally used for the spinels.

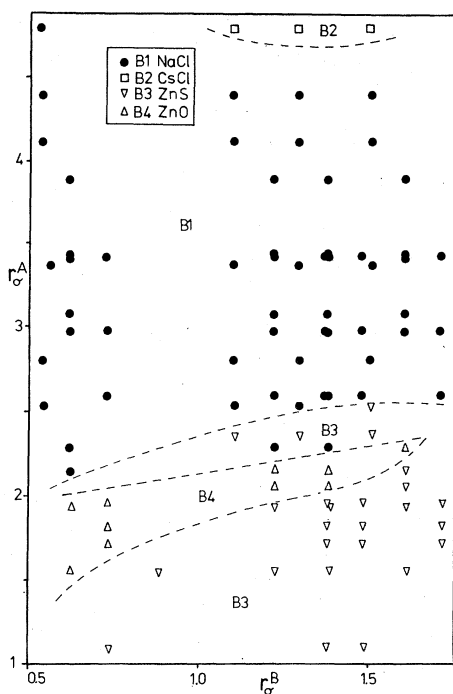


FIG. 2. Structural sorting map for AB octets using r_σ^A and r_σ^B as indices. A is the element at the left-hand side of the periodic table. The radii of Bloch and Schatteman (Ref. 4) are used. The data base (Ref. 6) consists of 99 examples, but (Sc,Y,La)Bi, with the NaCl structure lie off the right-hand side of the plot and are sorted correctly. The two errors are MgS and MgSe.

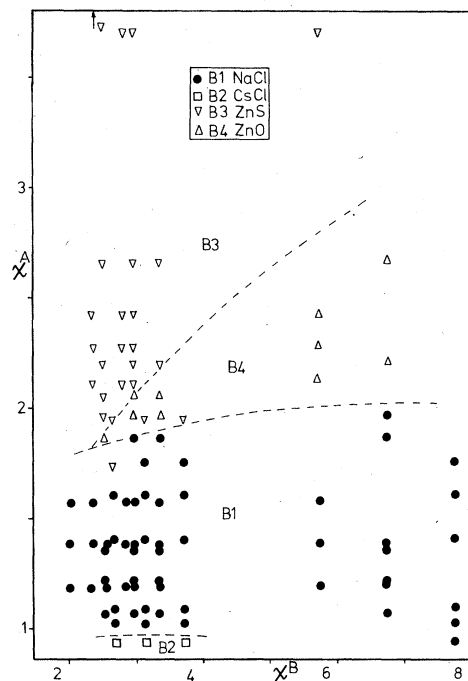


FIG. 3. Structural sorting map for AB octets using χ^A and χ^B , analogous to Fig. 2. The two errors in the $B4$ region are CuCl and CuBr, and the error in the $B1$ region is AgI. The (Sc,Y,La) X points are effectively coincident for $X = P, Se$.

neighbor level. We emphasize a point, often made, that such sorting is particularly impressive, since the energetic differences between the two geometrical arrangements are sometimes extremely small. We do note, however, that the structural sorting ability of these plots is largely determined simply by the ordering of the elements in terms of increasing r_σ or χ values, rather than the values themselves. The difference in the sorting ability of the r_σ and χ displays arises from a few slight changes in this ordering which prevents the χ plots from completely resembling an r_σ^{-1} plot. The empirical radii of Bloch and Schatteman (only available for a limited selection of elements) appear to be superior in this sorting ability to the first-principles radii.⁶ Note that the sorting in both Figs. 1 and 2 appears to be independent of whether the interaction between A and B would be traditionally described as "ionic" (large χ or r_σ difference) or covalent (small χ or r_σ difference).

AB_2 DOUBLE OCTETS

Figure 4 shows a crystal radii plot for these systems. As for the AB octets, the boundaries imposed by radius ratio considerations lead to a significant number of errors. The sorting can be drastically improved (Table I) by relaxing the location of the boundaries. Both an r_σ^A, r_σ^B plot (Fig. 5) and a χ^A, χ^B plot (Fig. 6) separate structural types well. There is a partial resolution of the cadmium iodide and chloride types although, for these structures, which polytype has the lower energy is often experimentally open to doubt. We do not include such cadmium halide "errors" in our summary of Table I. A dramatic sorting of the related octahedral (cadmium iodide) and trigonal prismatic (MoS_2) layer structures is also found. Parenthetically we note an earlier study of the problem,¹⁸ using a radius ratio and ionicity difference as structural indices, and also point out a somewhat less satisfactory sorting using the crystal radii in Fig. 4. Just as with the AB octets, the boundary is much more clearly defined using the pseudopotential compared to the crystal radii. The sorting, set once again by the ordering of the χ^ξ or r_σ^ξ , for these AB_2 double octets appears equally good irrespective of whether empirical or first-principles radii are used.

By way of contrast, an R_σ, R_π plot, using the definitions of Eqs. (1) and (2) or an R_σ, R'_π plot where $R'_\pi = r_\pi^A + 2r_\pi^B$, separate the structures very poorly indeed (Fig. 7). Fluorite and rutile, and rutile, cadmium halide, and molybdenite regions

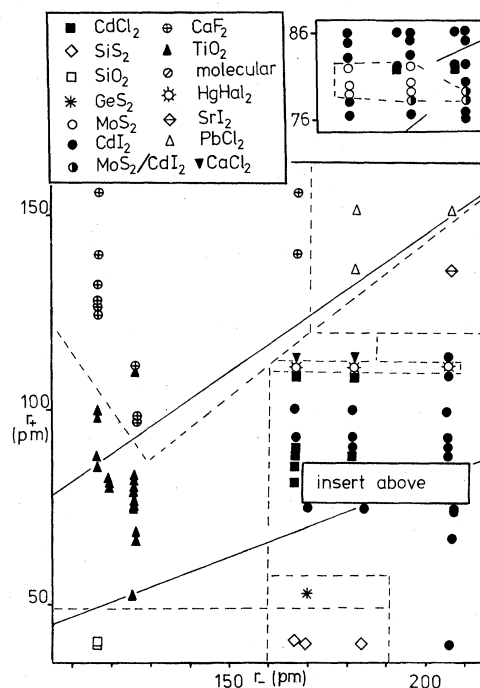


FIG. 4. Structural sorting for AB_2 double octets using crystal radii (Ref. 12) r_+ and r_- , appropriate to the observed coordination number. The solid lines represent the boundaries imposed by the radius ratio rules, and the dashed lines give optimal sorting. The AB_2 data base is culled from Refs. 17 and 18, and consists of 112 examples as shown in the Appendix. We do not distinguish between the different (and unique) structures adopted by the mercuric halides HgX_2 where $X = \text{Cl}, \text{Br}, \text{I}$. The three molecular AB_2 compounds cannot be included on this figure. Some compounds lie so close together on these AB_2 plots that they are represented by a single symbol.

overlap each other. The molecular solids, CO_2 , CS_2 , and N_2O appear between the very different SiO_2 and SiS_2 types. The SiO_2 type itself appears in the middle of the structurally unrelated cadmium halide field. The conclusion is perhaps a rather startling one. After the success of R_σ and R_π for AB systems, it is clear that these parameters do not mimic the factors responsible for structural preferences in AB_2 systems. This leads to the question as to why they work for the AB octets.

THE SPINELS, AB_2X_4

A rather different testbed for theoretical models of structural preference, which we discuss elsewhere¹⁹ in detail, is that of the cation distribution in the spinels. (This is one particular structure²⁰

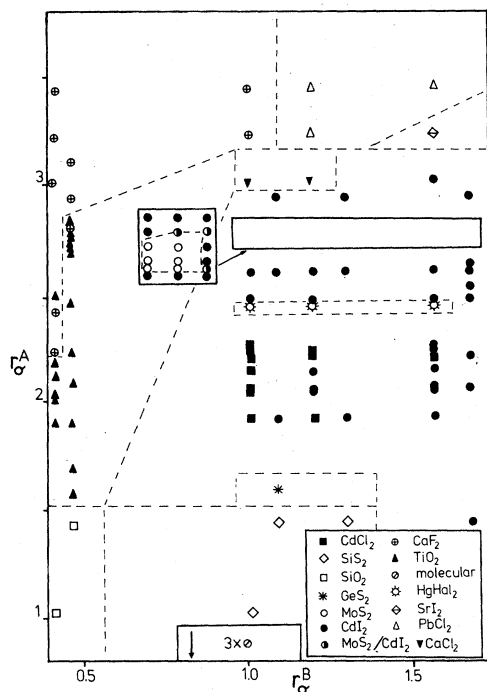


FIG. 5. Structural sorting map for AB_2 double octets using r_{σ}^A and r_{σ}^B as indices, and the radii of Zunger.⁶ The insert is drawn to a different scale and the three vertical columns represent sulfides, selenides, and tellurides. The species with the fluorite (CaF_2) structure located in the rutile (TiO_2) region at $r_{\sigma}^A = 2.825$ is ZrO_2 , which is polymorphic. The single obvious error is PdF_2 , which has the rutile structure but is found in the fluorite region of the plot. Such d^8 species are often distorted and, that its position is in error, is of no great concern.

adopted by materials of formula AB_2X_4 .) Figure 8 shows the sorting using $r_{\sigma}^A, r_{\sigma}^B$ of a large data base of 172 examples of this structural type into normal ($\{A\}[B_2]X_4$) and inverse ($\{B\}[A][B]X_4$) modifications. The brackets represent occupation of the octahedral sites and the braces occupation of the tetrahedral sites of a cubic-close-packed array of $X(O, S, Se, \text{ and } Te)$ atoms. Of the four obvious errors, in only two cases is the experimental data unequivocal in assigning a normal structure.¹⁹ In the others the evidence is not so reliable. An analogous sorting to that of Fig. 8 is achieved by using the $s + p$ electronegativity [Eq. (3)]. For these examples suitable crystal radii are scarce and only 48 compounds may be plotted using r_+^A and r_+^B as indices (Fig. 9). A poorer (Table I) sorting results. R_{σ}, R_{π} are also not good indices here.

This result is very interesting. Although it has always been recognized that s and p electrons prob-

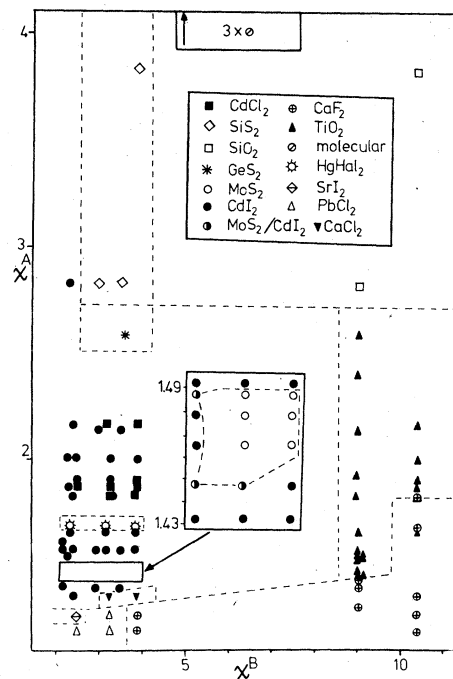


FIG. 6. Structural sorting map for AB_2 double octets using χ^A, χ^B as indices, analogous to Fig. 5. Again the rutile-fluorite error is PdF_2 .

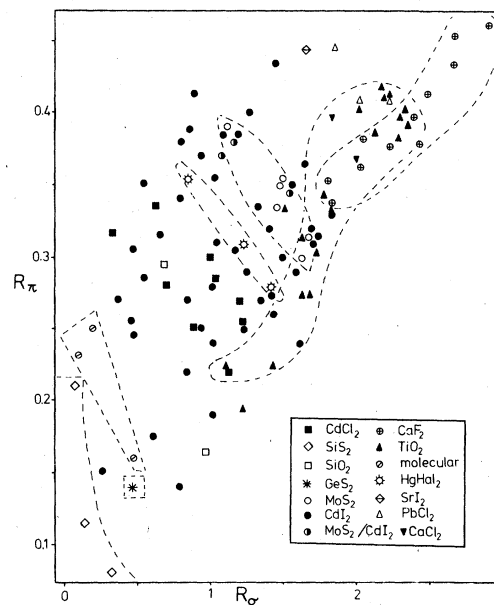


FIG. 7. Structural sorting map for AB_2 double octets using R_{σ} and R_{π} as indices, and Zunger's radii. The dashed lines have been included to help the reader collect together the majority of systems with the same structure.

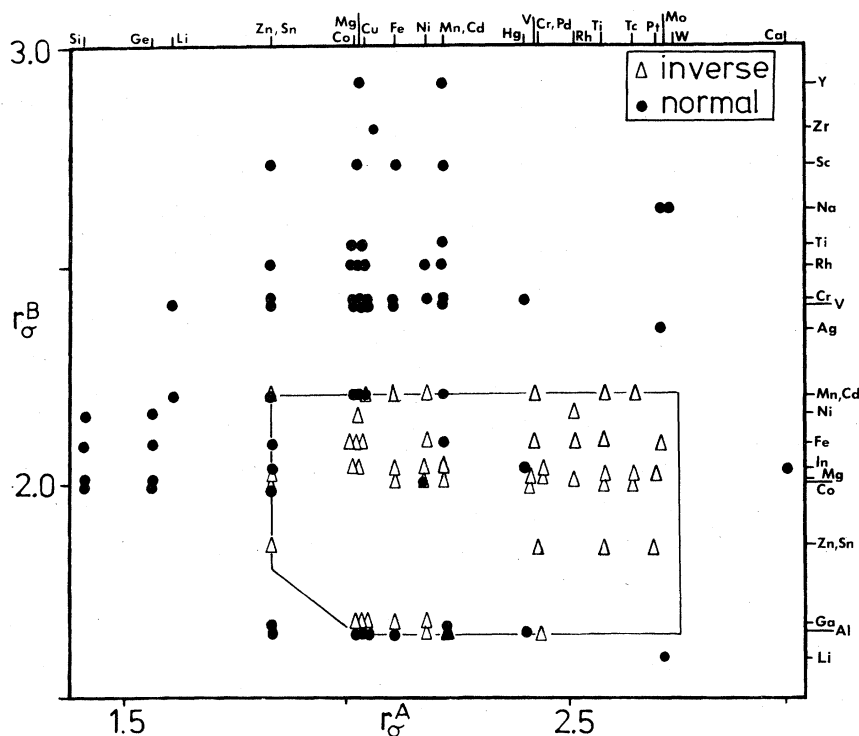


FIG. 8. Structural sorting map for spinels using r_A^A, r_B^B as indices and Zunger's radii (Ref. 6). The data base of 172 examples, is given in the Appendix and will be discussed in detail elsewhere (Ref. 25). The lanthanide examples, all of which have the normal structure lie off the top of the diagram. Several points represent more than one example, either because we do not distinguish the nature of X on this plot or because of the proximity of r_σ values for certain elements (e.g., Cr, Pd and Mn, Cd).

ably play an important role in this site-preference problem, the traditional textbook explanation of the problem uses the purely d -orbital-based crystal-field approach.²¹ Here the structure adopted is determined only by the crystal-field splittings

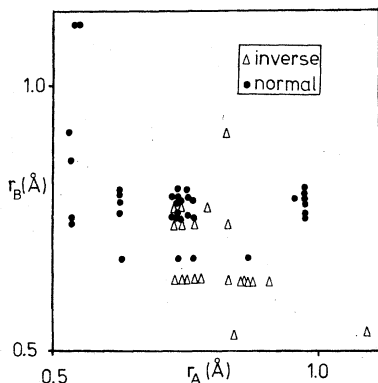


FIG. 9. Structural sorting map for AB_2X_4 spinels using the appropriate crystal ionic radii (Ref. 12) as indices, for the cases where such radii are available.

and the number of d electrons. From the data base of 172, there are only 74 spinels for which there are relevant spectral data and for which crystal-field theory can make a prediction. Sixty-one are correct. In our case we find¹⁹ that the compounds which lie on the borderline between the two regions of Fig. 8 are often disordered but that the extent of the disorder or the predominant structure is given correctly by the crystal-field theory. This sorting map suggests that s, p orbitals are much more important than d orbitals in determining the cation distribution, a conclusion very much more in accord with modern views²² of the transition-metal—ligand bond.

DISCUSSION

We briefly summarize the various indices which have been successfully used in structural sorting diagrams.

(i) The original² indices R_σ, R_π [Eqs. (1) and (2)] using pseudopotential radii are interpreted in terms

of a size or electronegativity mismatch (R_σ) and some measure of the orbital nonlocality (R_π). In this sense they resemble the indices [electronegativity difference and the average value (\bar{n}) of the principal valence quantum number] used by Mooser and Pearson¹ in their maps. Here \bar{n} is a measure of "metallicity" related to the atomic s - p energy separations. The rather uncertain way variations in the indices might determine the crystal structure does not give an immediate guide as to the definition of equivalent indices for problems of different stoichiometry. Maps using R_σ, R_π are excellent for AB compounds but are poor for both AB_2 systems and the spinel problem.

(ii) We discuss elsewhere²³ the generation of two new indices (T_1 and T_2), which describe numerically the energetic interactions between s and p orbitals in a solid structure where each atom is in an equivalent environment. (That is, where the structure and antistructure are identical.) T_1 describes the direct s - s and p - p interactions, T_2 describes the energetic contribution made by s - p mixing. The quality of the structural sorting is similar to that found using R_σ and R_π and indeed the analytic form of T_1 and T_2 are approximately related by a simple transformation to R_σ and R_π . This result underscores the current view that these two R parameters measure some sort of size or electronegativity mismatch (R_σ) and an orbital nonlocality (R_π), respectively. Thus R_σ takes care of the majority of the charge distribution between A and B , and R_π mainly measures the redistribution of charge between s and p orbitals on the same atom.

(iii) The results presented above using r_+ and r_- , suggest that the relative size of the ions, via their crystal radii may determine the structure, although we must discard the mechanical or radius ratio boundaries. These sorting maps are tolerable for AB and AB_2 systems.

(iv) A better sorting for AB, AB_2 , and AB_2X_4 may be obtained by replacing the crystal radii with a simple sum of atomic-orbital radii which are independent of oxidation state, coordination number, etc. These results suggest that "size" is very important and that the pseudopotential radii provide a better generalized size scale.

(v) The $s + p$ electronegativity χ^A, χ^B [Eq. (3)] sorts all three structural problems (probably better in fact than r_σ^A, r_σ^B , although it is difficult to estimate the quality of the sorting). The idea of electronegativity having a strong influence on structure (i.e., charge control) is well developed for molecular chemistry²² but is a relatively new one for solids.

Given these results, what do structural sorting diagrams tell us about the factors which are really important in determining crystal structures?

First we note that if a pair of indices give rise to structural sorting, they either directly describe the major factors which determine structural preference, or are related by an appropriate mapping of the true indices (which are a direct representation of the structure determining parameters), such that the topological clustering is preserved. Thus, the various pseudopotential related indices listed above which sort well for AB octets must be related to each other in this case. Second, we note the fundamental nature of the pseudopotential radii.

Although they do not correspond to any directly observable atomic size, by describing the "size" of the pseudopotential core experienced by the valence electrons, these radii directly determine orbital ionization potentials, and of course ionic, covalent, and van der Waals radii, etc. Hence, the relationship between the $\{r_i^\xi\}$ or the valence energy levels will closely control the covalent bonding possibilities between A and B . The atomic scales of both size and electronegativity have a long history of being conceptually useful, but only really in a qualitative fashion. Crystal chemists have used the rather vague concept of atomic (or ionic) size to provide rules of thumb for pigeonholing structures, for example, "crystals RX_2 in which R is especially big are likely to have the fluorite, CaF_2 arrangement".¹⁷ The present r_σ plots can quantify this much more precisely and sort better than crystal radii. The concept of electronegativity has been widely used by molecular chemists to view analogous site-preference problems in molecules.^{22,24} The most electronegative atoms generally occupy the sites of highest latent charge (generally those of lowest coordination). This is easy to understand. Since the total one-electron energy is given approximately $E = \sum q_i^\xi H_i^\xi$, where q_i^ξ is the charge in orbital i on atom ξ , and H_i^ξ the corresponding orbital ionization potential, the lowest-energy structure is found by the optimal matching of $\{q_i^\xi\}$ and $\{H_i^\xi\}$. If χ^A, χ^B plots sort solid-state structures because charge control determines the atomic site, and hence, structural preference, in an analogous way, then the r_σ^A, r_σ^B plots may be successful simply because of the relationship between χ^ξ and r_σ^ξ (or vice versa).

The fact that R_σ, R_π are successful for AB systems but not for AB_2 and AB_2X_4 is of paramount importance. It shows that the view of structural preference embodied in these parameters is only

valid for AB systems. The answer may lie in the observation that the AB octet structures contain A and B in identically coordinated environments but, in the AB_2 double octet structures, topological requirements prevent this. So whereas, r_σ^A, r_σ^B or χ^A, χ^B as indices may, because of their individual nature, allow structural resolution of different coordination geometries for A and B , use of the compound indices R_σ, R_π which both contain functions of the r_i^A and r_i^B may be too restrictive. In other words, use of r_σ^ξ or χ^ξ as indices will provide the necessary flexibility and freedom in a sorting map to find the best matching of $\{q_i^\xi\}$ and $\{H_{ii}^\xi\}$ as described above for any structure. Use of R_σ and R_π , coupled functions of r_i^A and r_i^B , should then work best for the case where the two sites have the same coordination number and local geometry. Here the site preference problem will be equally weighted by the nature of the A and B atoms.

Whether the structural preferences in these three systems, AB , AB_2 , AB_2X_4 are in fact determined by packing (size) or charge control (electronegativity) is in many ways an unanswerable philosophical question. They are both valid viewpoints although the failure of the mechanical model to describe structure does weigh against the former. They are, in fact, just models (with a physical significance of use in other areas of electronic structure) which combine the four atomic parameters $r_{s,p}^A, r_{s,p}^B$ into pairs of structural indices which might be expected to, and can sort structures in all three systems.

Clearly, however, the present approach is a very important and useful way of viewing global structural preference.

ACKNOWLEDGMENTS

We thank the donors of the Petroleum Research Fund for their partial support of this research. We are also grateful to the National Science Foundation for their support under Grant Nos. NSF CHE 7826579 and NSF DMR 8019741.

APPENDIX: DATA BASES AND ERRORS

Any compound which is misplaced on a sorting map using the optimum boundary lines is superscripted with the appropriate figure number. [Errors in Fig. 7 ($R_\sigma R_\pi$ for AB_2) and Fig. 9 ($r_+ r_+$ for AB_2X_4) are not included.]

AB octet compounds for Figs. 1, 2, and 3

B1 NaCl type

AgF, AgBr, AgCl, BaO, BaS, BaSe, BaTe
CaO, CaS, CaSe, CaTe, CdO, CsF, KF
KCl, KBr, KI, LaN, LaP, LaAs, LaSb, LaBi
LaO, LaS, LaSe, LaTe, LiF, LiCl, LiBr
LiI, MgO, MgS², MgSe², NaF, NaCl, NaBr
NaI, RbF, RbCl, RbBr, RbI, ScN, ScP
ScAs, ScSb, ScBi, ScS, ScSe, SrO, SrS, SrSe
SrTe, YN, YP, YAs, YSb, YBi, YO, YS
YSe, YTe

B2 CsCl type

CsCl, CsBr, CsI

B3 ZnS type—"zinc blende"

AgI^{1,3}, AlP, AlAs, AlSb, BN, BP
BaS, BeS, BeSe, BeTe, CsI, CdTe¹
CuCl³, CuBr³, CuI, GaP, GaAs, GaSb
HgTe¹, InP, InAs, InSb, ZnS, ZnSe
ZnTe

B4 ZnO-type "wurtzite"

AlN, BeO, CdS¹, CdSe¹, GaN, HgS¹
HgSe¹, InN, MgTe, ZnO

AB₂ double octet compounds for Figs. 4, 5, 6, and 7

CdCl₂ type

CdCl₂, CdBr₂, CoCl₂, FeCl₂, MgCl₂
MnCl₂, NiBr₂, NiCl₂, NiI₂, ZnCl₂
ZnBr₂

CaF₂-type "fluorite"

BaF₂, BaCl₂, CaF₂, CdF₂, CeO₂,
HfO₂, HfF₂, SrF₂, SrCl₂, ZrO₂⁵

<i>SiS₂ type</i>	<i>CaCl₂ type</i>
BeCl ₂ , SiS ₂ , SiSe ₂	CaCl ₂ , CaBr ₂
<i>TiO₂-type "rutile"</i>	<i>Unique structures</i>
CoF ₂ , CrO ₂ , GeO ₂ , FeF ₂ , IrO ₂ , MgF ₂ MnF ₂ , βMnO ₂ , MoO ₂ , NbO ₂ , NiF ₂ OsO ₂ , PbO ₂ , PdF ₂ ^{5,6} , RuO ₂ , SnO ₂ TaO ₂ , TeO ₂ ⁴ , TiO ₂ ⁴ , WO ₂ , ZnF ₂	GeS ₂ , SrI ₂
<i>SiO₂ type</i>	<i>AB₂X₄ Spinels for Figs. 8 and 9</i>
BeF ₂ , SiO ₂	This compilation does not include A ₃ X ₄ spinels, and the small number of spinels where X is not a chalcogen. These are discussed elsewhere. ²⁵
<i>Molecular</i>	<i>Predominantly normal</i>
CO ₂ , CS ₂ , ON ₂	Li(V,Mn) ₂ O ₄ , Mg(Al,Ti,V,Cr,Mn,Rh) ₂ O ₄ , Si(Mg,Fe,Co,Ni) ₂ O ₄ Ge(Mg,Fe,Co,Ni) ₂ O ₄ , Cu(Al,Cr,Mn,Rh) ₂ O ₄ , Zn(Al,Ga,V,Cr,Mn,Fe,Co,Rh) ₂ O ₄ , Cd(Ga,V,Cr,Mn,Fe ⁸ ,Rh) ₂ O ₄ , Mo(Li,Na,Ag) ₂ O ₄ , WNa ₂ O ₄ Mn(Al,Ga,Ti,V,Cr,Fe ⁸ ,Rh) ₂ O ₄ , Fe(Al,V,Cr) ₂ O ₄ Co(Al,V,Cr,Mn,Rh) ₂ O ₄ , Ni(Cr,Rh) ₂ O ₄ Mg(Sc,Tm,Yb,Lu) ₂ S ₄ CaIn ₂ S ₄ , Cu(Ti,Zr,V,Cr,Rh) ₂ S ₄ Zn(Al,In,Sc,Cr) ₂ S ₄ , Cd(Al,Y,Cr,Ho,Er,Tm,Yb,Lu) ₂ S ₄ Hg(Al,In ⁸ ,Cr) ₂ S ₄ , Mn(Sc,Cr,Tm,Yb,Lu) ₂ S ₄ Fe(Sc,Cr,Yb,Lu) ₂ S ₄ , Co(Cr,Rh) ₂ S ₄ , Ni(Co ⁸ ,Rh) ₂ S ₄ Mg(Sc,Y,Ho,Er,Tm,Yb,Lu) ₂ Se ₄ , Cu(Cr,Rh) ₂ Se ₄ Zn(Al,Cr) ₂ Se ₄ , Cd(Al,Y,Cr,Dy, Ho,Er,Tm,Yb,Lu) ₂ Se ₄ Hg(Al,Cr) ₂ Se ₄ , Mn(Sc,Yb,Lu) ₂ Se ₄ , CuCr ₂ Te ₄ ZnMn ₂ Te ₄
<i>Mercury halide</i>	<i>Predominantly inverse</i>
HgCl ₂ , HgBr ₂ , HgI ₂	Mg(Ga,In,Fe) ₂ O ₄ , Sn(Mg,Zn,Cd,Mn,Co) ₂ O ₄ Cu(Ga,Fe) ₂ O ₄ , Cd(Al,In) ₂ O ₄ , Ti(Mg,Zn,Mn,Fe,Co) ₂ O ₄ V(Mg,Zn,Mn,Fe,Co) ₂ O ₄ , Cr(Mn,Fe) ₂ O ₄ MoFe ₂ O ₄ , MnCo ₂ O ₄ , Tc(Mg,Mn,Co) ₂ O ₄ Fe(Ga,Mn,Co) ₂ O ₄ , Co(Ga,Fe) ₂ O ₄ Ni(Al,Ga,Mn,Fe,Co) ₂ O ₄ , PdMg ₂ O ₄ Pt(Mg,Zn) ₂ O ₄ , MgIn ₂ S ₄ , Cr(Al,In) ₂ S ₄ FeIn ₂ S ₄ , Co(In,Ni) ₂ S ₄ , Rh(Fe,Co,Ni) ₂ S ₄ NiIn ₂ S ₄
<i>PbCl₂ type</i>	
BaBr ₂ , BaI ₂ , SrBr ₂	
<i>CdI₂ type</i>	
CaI ₂ , CdI ₂ , CoBr ₂ ⁴ , CoI ₂ , CoTe ₂ FeBr ₂ , FeI ₂ , HfS ₂ , HfSe ₂ , HfTe ₂ IrTe ₂ , MgBr ₂ , MgI ₂ , MnBr ₂ , MnI ₂ NiTe ₂ , NbTe ₂ , PdTe ₂ , PtS ₂ , PtSe ₂ PtTe ₂ , RhTe ₂ , SiTe ₂ , SnS ₂ , SnSe ₂ , TaTe ₂ TiCl ₂ , TiBr ₂ , TiI ₂ , TiS ₂ , TiSe ₂ TiTe ₂ , VCl ₂ , VBr ₂ , VI ₂ , VS ₂ VSe ₂ , VTe ₂ , WTe ₂ , ZnI ₂ , ZrS ₂ ZrSe ₂ , ZrTe ₂	
<i>MoS₂ type</i>	
MoS ₂ , MoSe ₂ , NbS ₂ , NbSe ₂ , WS ₂ , WSe ₂	
<i>MoS₂ and CdI₂ structures</i>	
MoTe ₂ , TaS ₂ , TaSe ₂	

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- ¹E. Mooser and W. B. Pearson, *Acta Crystallogr.* **12**, 1015 (1959).
- ²J. St. John and A. N. Bloch, *Phys. Rev. Lett.* **33**, 1095 (1974).
- ³J. C. Phillips, *Comments Solid State Phys.* **9**, 11 (1978).
- ⁴A. N. Bloch and G. C. Schattman, in *Structure and Bonding in Crystals*, edited by A. Navrotsky and M. O'Keeffe (Academic, New York, 1981).
- ⁵A. Zunger, *Phys. Rev. Lett.* **44**, 582 (1980).
- ⁶A. Zunger, *Phys. Rev. B* **22**, 5839 (1980).
- ⁷J. R. Chelikowsky and J. C. Phillips, *Phys. Rev. B* **17**, 2453 (1978).
- ⁸E. S. Machlin, T. P. Chow, and J. C. Phillips, *Phys. Rev. Lett.* **38**, 1292 (1977).
- ⁹A. Zunger, in *Structure and Bonding in Crystals*, edited by A. Navrotsky and M. O'Keeffe (Academic, New York, 1981).
- ¹⁰L. Pauling, *The Nature of the Chemical Bond*, 4th ed. (Cornell University Press, Ithaca, 1960).
- ¹¹J. C. Phillips, in *Treatise on Solid State Chemistry*, edited by N. B. Hannay (Plenum, New York, 1974), Vol. I.
- ¹²R. D. Shannon, *Acta Crystallogr. Sec. A* **32**, 751 (1976).
- ¹³M. Natapoff, *Chem. Phys. Lett.* **78**, 375 (1981).
- ¹⁴G. Simons and A. N. Bloch, *Phys. Rev. B* **7**, 2754 (1973).
- ¹⁵A. Zunger and M. L. Cohen, *Phys. Rev. Lett.* **41**, 53 (1978).
- ¹⁶W. Andreoni, A. Baldreschi, E. Biemont, and J. C. Phillips, *Phys. Rev. B* **20**, 4814 (1979).
- ¹⁷R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1965).
- ¹⁸F. R. Gamble, *J. Solid State Chem.* **9**, 358 (1974).
- ¹⁹J. K. Burdett, G. D. Price, and S. L. Price (unpublished).
- ²⁰R. Roy and O. Muller, *The Major Ternary Structural Families* (Springer, New York, 1976).
- ²¹T. M. Dunn, D. S. McClure, and R. G. Pearson, *Aspects of Crystal-Field Theory* (Harper and Row, New York, 1966).
- ²²J. K. Burdett, *Molecular Shapes* (Wiley, New York, 1980).
- ²³J. K. Burdett and S. L. Price (unpublished).
- ²⁴R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.* **98**, 2484 (1976).
- ²⁵G. D. Price, S. L. Price, and J. K. Burdett (unpublished).