PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Determination of AB crystal structures from atomic properties

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(Received 1 July 1988)

We use atomic pseudopotential s-orbital radii and Pauling electronegativity χ to distinguish between four types of crystal structures (ZnS, NaCl, CsCl, and MnP or NiAs) for AB compounds. By relating χ to the s-orbital radii, an even simpler scheme results, indicating the important role of pseudopotential s-orbital radii for structural determination.

The analyses of crystal structures using atomic properties have been refined during the last decade. In early semiclassical approaches,[1-3] phenomenological scales such as empirical radii and electronegativities were constructed to characterize bonding and structural properties. The major advantage of empirical scales is that they are easy to apply and intuitive. Hence, this approach has been used both to study chemically complicated systems, for which first-principles calculations are prohibitive, and for examining trends between bonding and structure. Some approaches use a combination of atomic and solid properties such as the recent study[4] of relations among structures, cell dimensions, and the size of the constituent atoms. However, most of the recent developments[5-13] involve microscopic approaches closer to first principles. These schemes are usually based on more fundamental properties such as effective atomic numbers[6] and atomic-orbital radii.[8,14,15]

One of the approaches based on microscopic radii uses an *ab initio* pseudopotential calculation to obtain orbital radii. These radii are used to construct atomic coordinates which separate the structures of non-transition-element AB octets[7] and nonoctets with transition-metal compounds.[8] In a recent study,[10] these coordinates, together with the electronegativity and atomic valences,are used to separate more than 3000 intermetallic compounds with a success rate near 97%. This scheme was also applied to two more-complicated novel systems, quasicrystals[12] and high-temperature superconductors.[13]

The search for an optimum scheme for constructing and explaining structure maps from microscopic theory has resulted in several useful suggestions using combinations of s- and p-orbital radii. Some schemes yield structure maps of s- and p-orbital radii which have been successful but lack significant *a priori* justification. For example, the Zunger-Cohen[7] scheme uses the following combination of s- and p-orbital radii proposed by Simons and Bloch[9] for AB compounds:

$$\begin{aligned} r_\pi^{AB} &= |(r_p - r_s)|_A + |(r_p - r_s)|_B \; , \\ r_\sigma^{AB} &= |(r_p + r_s)_A - (r_p + r_s)_B| \; . \end{aligned} \tag{1}$$

Part of the rationale for these choices is the belief that the structural stability of an AB compound is closely related to the separation between s and p atomic energy levels. This argument is used explicitly in Eq. (1). One can argue that r_π scales with the atomic s and p energy difference and to some extent measures s-p hybridization, while r_σ gives a measure of the size difference between atoms which roughly scales with ionicity. Hence, the hybrid of atomic s- and p-orbital radii in r_π and r_σ were considered as basic to the success of the Zunger-Cohen scheme.[7] Slightly different definitions for r_π and r_σ have been proposed but the underlying assumptions[15] are similar.

In contrast with the above approach, it was shown recently that the pseudopotential s-orbital radii are linearly correlated with the bond lengths of AB octets regardless of the sizes of the p-orbital radii.[16] This raises the question of whether some of the previous views of the role of atomic radii in structural separations, although intuitive, are inadequate or incomplete. Since any phenomenological scale which produces the correct one-dimensional Mendeleev-type ordering of the elements could lead to structural separation to some extent,[6] a successful structure scheme should also simultaneously handle correctly the quantum-mechanical bonding. Accordingly, we propose a new scheme for constructing structure maps which, consistent with Ref. 16, has no explicit dependence on the p-orbital radii.

The successes of the present scheme suggest that the structural separations of AB compounds achieved in the earlier approach[7] are not caused by the choice of a proper hybrid of the s- and p-orbital radii but rather by the fact that r_s determined in a pseudopotential approach characterizes the balance between the nonclassical repulsive Pauli core potential and the attractive core-valence Coulomb potential screened by valence electrons—a feature unique to *pseudopotential* s-orbital radii. This view is suggested by the linear relation[16] between r_s and bond lengths, and by the definition of r_s which is a measure of the cancellation between the spherical repulsive and attractive potentials.[7,8]

A data base[17] of nearly 400 AB compounds is used and we follow the classification[18] of separating AB compounds into octet, superoctet, and suboctet compounds. The goal here is to demonstrate the importance of the atomic pseudopotential s-orbital radii in structural separations instead of giving a comprehensive survey of structure maps. Only four basic structures will be discussed.

These are the fourfold ZnS (including diamond and wurtzite), sixfold NaCl, and eightfold CsCl. We also include sevenfold-coordinated MnP and NiAs as *AB* suboctet systems. The latter two structures cannot be distinguished from each other in the present scheme. Nonetheless, the success of our approach is impressive since the structural energy differences are so small—only a few hundredths of their binding energies.

We define a violation in the present scheme as follows: (i) a violation occurs when a compound with one structure is located in a region assigned to another structure; (ii) no violation occurs when compounds with either structure lie on the boundary of two different structures; (iii) no violation occurs in regions where two or three phases overlap.

Figure 1 contains a structure map for 114 *AB* octets.[19] The coordinates are the pseudopotential *s*-orbital radii for the cation, r_s^c, and the pseudopotential *s*-orbital radii for the anion, r_s^a. The cation and anion are distinguished by their electronegativities.[1] The condition $r_s^c = r_t = 0.98$ a.u. separates the ZnS from the NaCl structures, and $r_s^c = r_t' = 1.67$ a.u. separates the NaCl from the CsCl. A similar trend holds for 18 superoctets where $r_s^c = 0.9$ a.u. separates the NaCl from the CsCl structure. Since there is no structural dependence on r_s^a, Fig. 1 is in fact one dimensional. The difference between the octet and superoctet systems can be attributed to the fact that more electrons which prefer a higher coordination number are involved in bonding in the superoctet and this effectively reduces the stability of the NaCl structure. There are three violations in Fig. 1. These are AgI, MgO, and CdO. According to our scheme, MgO would have the ZnS structure, AgI would have the NaCl structure, and CdO would have the ZnS structure. The r_s^c values of the latter two are very close to the separating boundary r_t between ZnS and NaCl structures, making the separations more subtle. A total success rate of about 98% is achieved.

In previous radii schemes, the roles of the cations and anions are mixed. In contrast, Fig. 1 shows that these roles can be distinguished. Structural stability is governed by the cation *alone* for the *AB* octet and this agrees with recent *ab initio* pseudopotential studies of the pressure-induced structural changes of nine group III-V element compounds.[20]

For the *AB* suboctets, we introduce another set of coordinates, the Pauling electronegativity χ^c for the cation and r_s^a, the *s*-orbital radii for the anion. The structure map for 255 *AB* suboctets is given in Fig. 2. For $r_s^a = r_t = 0.54$ a.u. the NaCl structures separate from the MnP and NiAs structures and at $r_s^a = r_t' = 0.8$ a.u. there is a separation of the MnP and NiAs structures from the CsCl structures. Most of the *AB* suboctets are metals. In contrast, *AB* octets are qualitatively different and most of them are insulators and semiconductors. Since the valence bands have mainly anionic character, whereas the lowest conduction band has more cationic character, it is plausible that the charge environment of the anions bear more chemical similarities in octets which have filled valence bands than in suboctets. One noticeable feature of the present scheme is that all the separations occur at lines perpendicular to one of the axes. This is useful in searching for the microscopic origins of the separations. For example, all the first-row compounds with small r_s^a have the NaCl structure. The coordination number increases from sixfold to sevenfold to eightfold as r_s^a, which measures the size of the anion, increases for relatively small χ^c. However, when the cation can have more electrons, the sevenfold structure remains at relatively large r_s^a. The separation occurs at $\chi_t = 1.8$ which is characteristic of this saturation.

There are two violations in the 255 suboctets. These are MnBi (which has unidentified phase $P2_1/m$) and AuGa. A success rate of 99.2% is achieved. Compounds listed by Villars[17] but not included in Fig. 2 are given in Table I where we also list the conditions under which they were found. We believe that including these compounds is not appropriate; nevertheless, their inclusion only reduces the success of the present scheme by less than 2%.

There are 38 compounds in Fig. 2 with $r_s^a \geq 0.8$ and

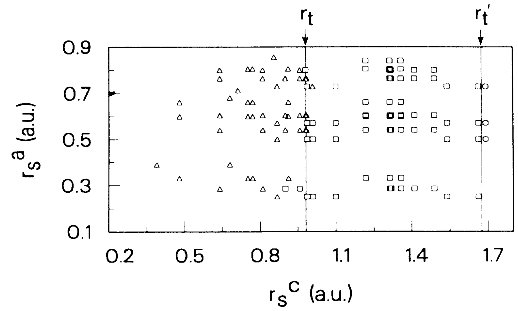

FIG. 1. Structure map for 114 *AB* octets: 48 ZnS (triangles), 63 NaCl (squares), and 3 CsCl (circles). The coordinate r_s^c is the pseudopotential *s*-orbital radius of the cation and r_s^a is the pseudopotential *s*-orbital radius of the anion. Structural separations occur at r_t and r_t'.

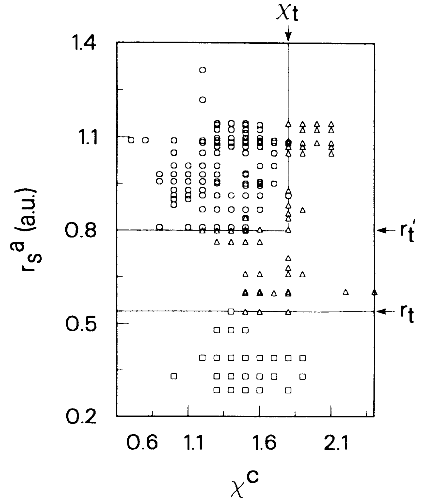

FIG. 2. Structure map for 255 *AB* suboctets: 38 NaCl (squares), 86 MnP or NiAs, (triangles) and 131 CsCl (circles). The coordinate χ^c is the Pauling electronegativity and r_s^a is the pseudopotential *s*-orbital radius of the anion. Structural separations occur at r_t, r_t', and χ_t.

TABLE I. Six *AB* compounds not included in Fig. 2. The low- and high-temperature phases are indicated by LT and HT.

Substances	Structures
ZrP	TiAs (LT), NaCl (HT)
RuSi	CsCl (HT)
AlSc	CsCl (1073-K, 4-h anneal)
BeTi	CsCl (metastable)
OsSi	FeSi, Cscl (chem. anneal)
AlY	BCr (LT), CsCl (HT)

$\chi^c \geq \chi_t = 1.8$ for which the value of χ^c is crucial and makes the distinction between the CsCl and the MnP or NiAs structures. To reduce the dependence on the empirical parameter χ, we plot in Fig. 3 the correlation between $\bar{\chi}$ and $Z_v e^2/r_s$ for 35 simple elements with valences from one to seven. The simple elements refer to the elements in the I*A*, II*A*, and III*B*–VII*B* columns of the first five rows of the Periodic Table. Z_v is the valence and $\bar{\chi}=\chi-0.2$ represents the electronegativity with a new origin (the origin of χ is arbitrary). A simple functional form

$$\bar{\chi}=\frac{1}{2}\left[\frac{Z_v e^2}{r_s}\right]^{1/2} \tag{2}$$

is established[21] by a least-squares fit with a rms percentage error of 5% (solid curve in Fig. 3).[22] From our previous discussion, it is not surprising that Eq. (2) is qualitatively different from an earlier study[23] of χ which assumed a linear relation between χ and the inverse of r_l for $l=s,p,d$. Equation (2) is limited to the simple elements because of the difficulties in defining an effective charge Z_v for valence *d* electrons from first principles. Nonetheless, there are 30 out of the 38 compounds (about 80%) with simple element cations which dominate the separation at χ_t. Thus Eq. (2) to a large extent eliminates the need for empirical data for the suboctets.

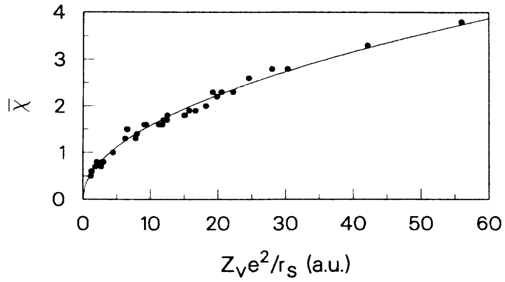

FIG. 3. Pauling electronegativity $\bar{\chi}$ vs $Z_v e^2/r_s$ for 35 nontransition elements.

In conclusion, we find that the pseudopotential *s*-orbital radii r_s can be used effectively as structural coordinates. Including the empirically determined electronegativity χ yields further separations. By relating χ to r_s, the need for empirical data is removed for a subset of elements.

We wish to thank Dr. J. C. Phillips for stimulating discussions. This work was supported by National Science Foundation Grant No. DMR83-19-024 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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[18] By definition, an octet has eight valence electrons, a superoctet has more than eight valence electrons (sometimes ten valence electrons) and a suboctet has less than eight valence electrons. When transition elements are involved, the classification for the octet and suboctet is not always unique (Ref. 4).

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