Zeitschrift: Helvetica Physica Acta
Band: 58 (1985)
Heft: 2-3

Artikel: Structure and properties : Mooser-Pearson plots
Autor: Phillips, J.C.
DOI: https://doi.org/10.5169/seals-115590

Nutzungsbedingungen
Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation
L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use
The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 26.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Helvetica Physica Acta, Vol. 58 (1985) 209–215 0018–0238/85/020209–07$1.50 + 0.20/0
© Birkhäuser Verlag Basel, 1985

Structure and Properties: Mooser–Pearson plots

By J. C. Phillips, AT&T Bell Laboratories, 1D-371 Murray Hill, New Jersey 07974

(15. IV. 1984)

In honor of Emanuel Mooser's 60th birthday

Abstract. The enclosed paper reviews some remarkable recent advances, chiefly due to Villars, in our understanding of chemical bonding in solids as derived from global structural diagrams.

Our knowledge of the structures and properties of solids has advanced enormously since 1959, when Mooser and Pearson showed [1] how ionic and metallic effects compete to differentiate closely similar structures with densities differing typically by 1%. That year I had the good fortune to visit the National Research Council in Ottawa, where Mooser and Pearson explained their new ideas. Although inexperienced I still realized the importance of their work, and I resolved that 'someday' I would understand it! The eventual achievement of that goal represented a milestone in the development of my own understanding of science in general and chemical bonding in particular.

Even in 1959 I realized that most attempts to separate structures of many similar alloys and compounds on Cartesian plots using two structural coordinates fail, and fail badly. A prototypical example is the famous 'radius ratio' model of binary ionic crystals, applied to the alkali halides M^+X^-, which are the simplest case. It has been traditional since Madelung and Born to idealize these ions as nearly incompressible spheres (isoelectronic to inert gases) interacting attractively through Coulomb potentials. When the cation and anion radii are equal, $r_+/r_- = \rho = 1.00$, the most favorable crystal structure is CsCl (coordination number = CN = 8). As ρ decreases, the anions come into contact, and CN = 6 is favored below $\rho = 0.732$, and then CN = 4, below $\rho = 0.414$. The actual crystal structures are shown in Fig. 1. The agreement of the radius model with experiment is poor [2].

The rationalization for this failure is that structural energy differences are too small to calculate and so no successful theory is possible. Mooser and Pearson did not accept this excuse. Instead they enlarged the universe of discourse to include all A^NB^{8-N} compounds from NaCl ($N = 1$) to Si and Ge ($N = 4$). They also introduced new coordinates, not of the hard sphere type, to describe how ionic potential energies (measured by the Pauling electronegativity difference ΔX) compete with kinetic energies (measured by the average principal quantum number $\bar{n}$) to determine structure. This is a very successful plot indeed, compared

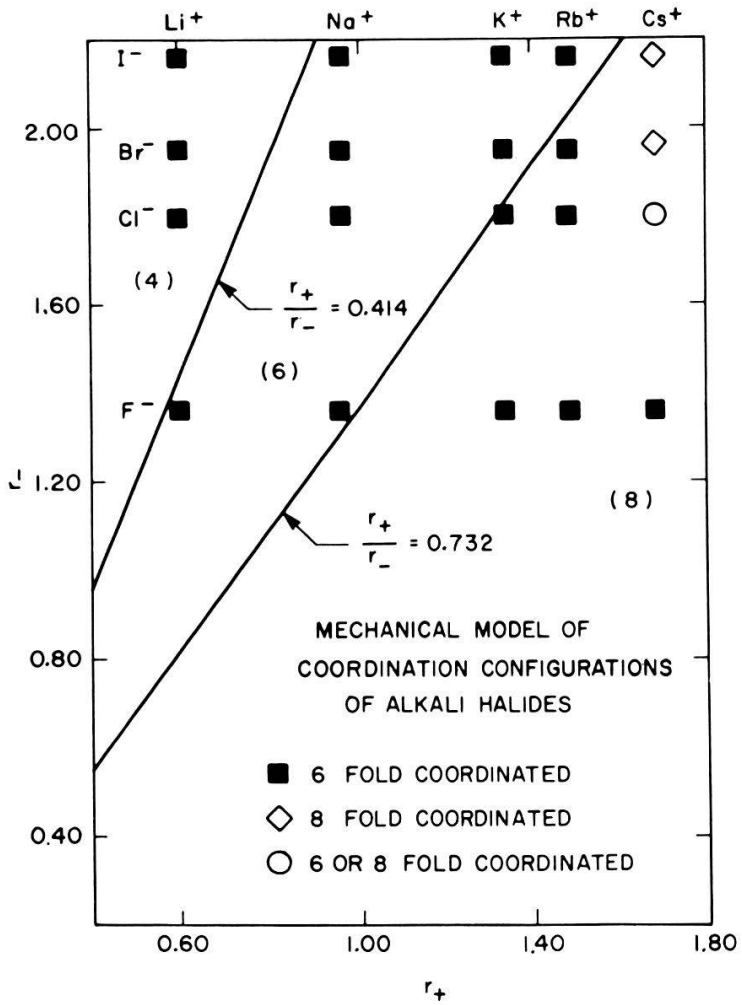
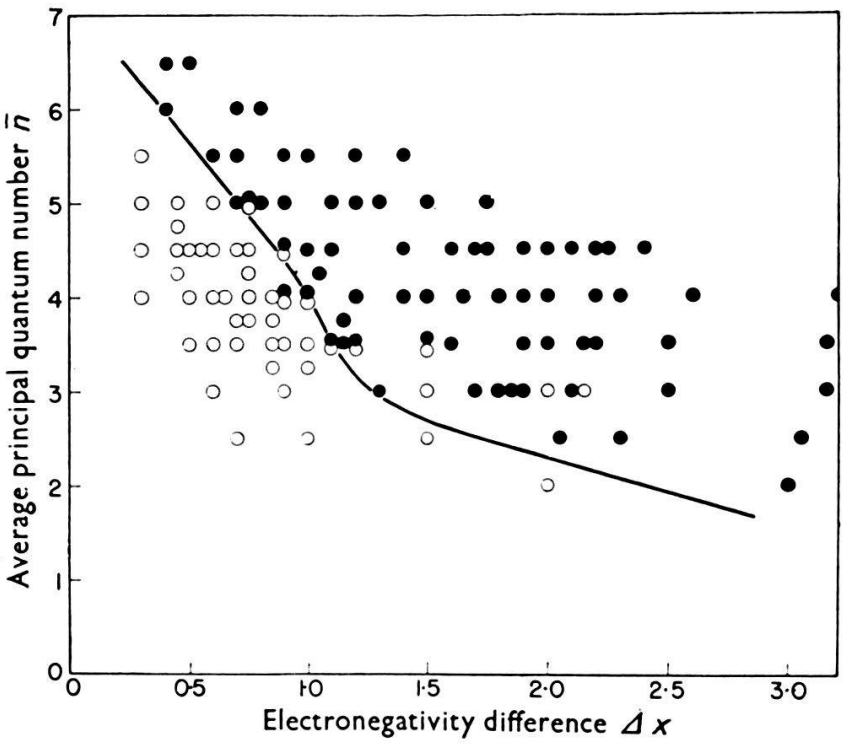


Figure 1
A Cartesian plot using cation and anion radii r_+ and r_- to exhibit actual crystal structures of the alkali halides, and contrast them with the predictions of the mechanical model where phase transitions to lower coordination numbers occur when the rigid ions establish second-neighbor contacts. For $r_+/r_- > 0.732$ the (8)-fold coordinated CsCl structure is predicted to be stable, and so on. Note the poor agreement between experiment and the classical mechanical model.

to Fig. 1. Mooser and Pearson went on [1] to discuss successfully transition metal compounds as well.

As is so often the case for simple and general ideas, this early work of Mooser and Pearson's soon became widely known, but for a while it was little imitated, so little in fact that it appears to have been well ahead of its time. I am proud to say that when the next important step came, it was ten years later as a consequence of my efforts to compress the results of many quantum-mechanical pseudopotential calculations into an algebraically simple form similar to the Hückel molecular orbital theory of conjugated hydrocarbons. My theory [3] utilized dielectric constants ϵ. The crystalline analogue of the atomic f-sum rule was used to eliminate oscillator strengths and estimate average energy gaps between occupied and empty states. This average energy gap E_g was separated into covalent and ionic components, E_h and C respectively, by a Hückel relation $E_g^2 = E_h^2 + C^2$. One could then determine E_h and C separately by scaling the former with the bond length d and obtain E_g and C from ϵ. In this model the transformation from tetrahedral to octahedral coordination depends on the fraction of ionic character in the chemical bond given by $f_i = C^2/E_g^2$. The results are



○ B3, B4, $E1_1$ tetrahedral coordination.
● B1 octahedral coordination.

Figure 2
The original Mooser–Pearson plot for $A^N B^{8-N}$ compounds (Ref. 1). Filled circles: 6-fold coordinated compounds, empty circles, 4-fold coordinated compounds. Included on the plot in addition are transition metal compounds TX (such as transition metal carbides). These account for most of the errors (octahedral compounds in tetrahedral area).

shown in Fig. 3. The separation of structures is perfect (no errors) and utilizes only a straight line [4], $f_i = 0.785 \pm 0.015$.

One of the advantages of diagrammatic analysis is that one can often use the patterns to infer the effects of different choices of structural variables. The ionic energy gap C is very similar to Pauling's electronegativity difference ΔX. Thus it appears that the difference between the Mooser–Pearson plot and the Phillips–Van Vechten plot is contained in the difference between $\bar{n}$ and E_h. As stated by Mooser and Pearson, they introduced $\bar{n}$ as a rough measure of band width (kinetic energy) or 'metallization'. For this problem E_h is a more refined index measuring essentially the same effect, but in a more accurate way which is also more directly comparable to the way C measures ionic effects.

By comparing Mooser–Pearson and Phillips–Van Vechten structural diagrams we can see that indeed the structural patterns are determined by small energy differences and that the ability of certain coordinates to describe these differences is in itself highly informative. Many analytic calculations are carried through very elaborately on one or two compounds, and yet at the end one cannot say with much confidence how accurate the results are. Conversely, the simple geometries of Cartesian structural plots (such as those shown in this paper) concerning, e.g., 80 $A^N B^{8-N}$ compounds, have turned out to be genuinely instructive in a way that even Mooser and Pearson could not have suspected in 1959.

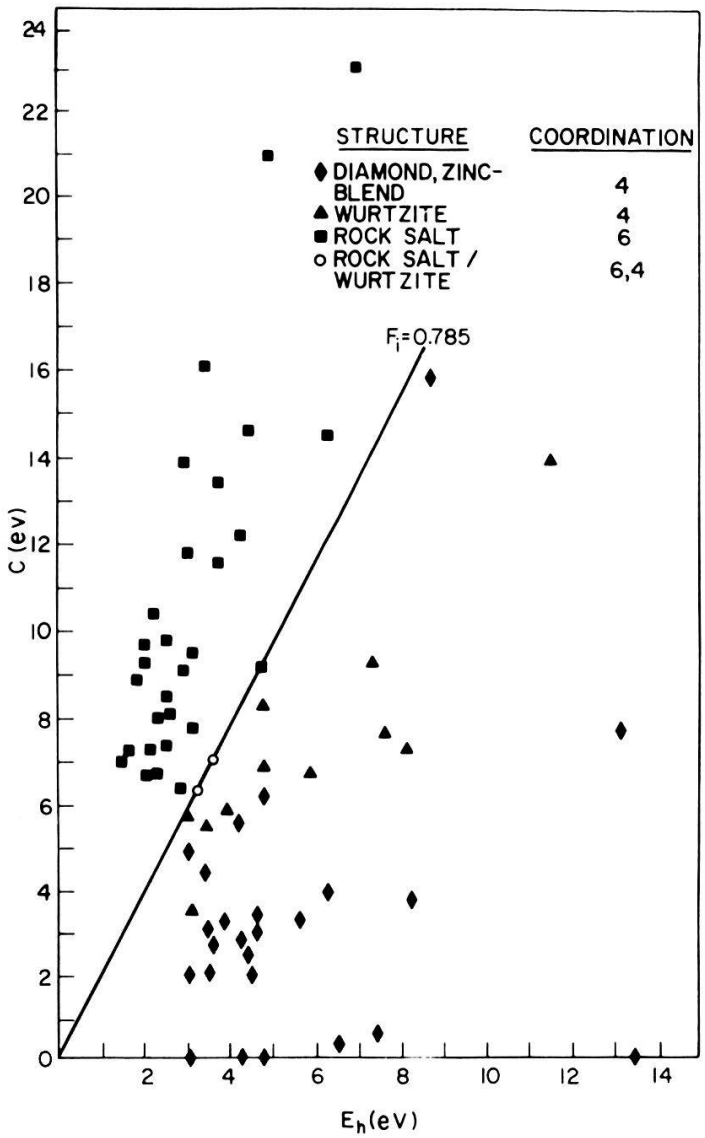


Figure 3
The Phillips–Van Vechten plot for $A^N B^{8-N}$ valence compounds utilizing 'symmetric' energy-gap coordinates E_h and C. The use of quantum-mechanically defined coordinates, together with the restriction to valence compounds and exclusion of transition-metal compounds, leads to an exact separation with a straight line corresponding to constant critical ionicity.

Following the success of the Phillips–Van Vechten $A^N B^{8-N}$ structural analysis using dielectric theory, interest in Cartesian structural analysis in the Mooser–Pearson spirit grew rapidly. I reviewed [4] many of these developments in 1977. Particularly successful were the analyses made using 1-dependent ($1 = 0, 1$, i.e., s- and p-) orbital radii as defined from atomic term levels by Bloch and coworkers [5]. One of my favourite examples which demonstrates the power of these radii for structural analysis is given by the family of intermetallic compounds crystallizing in the CrB structure. This structure contains spiral chains of B atoms with eight atoms/unit cell. The eminent crystallographer E. Parthe stated [6] that 'Simple ideas on crystal structure formation using size effects, number of valence electrons, etc., are just not sufficient' for explaining structural trends in the CrB family. This makes the result [7] shown in Fig. 4 for the helical pitch angle of the spiral chains in compounds having the CrB structure especially

satisfying, because the pitch angles are correlated with an accuracy of better than 0.5° for 10 different metal-metalloid compounds. The exception on this plot, CaAg, is a well-known catalyst and is probably not stoichiometric. Incidentally, Fig. 4 is the most sophisticated result obtained using orbitally dependent radii. These orbital coordinates were tested on a number of other simpler and by now standard structural problems, including the $A^N B^{8-N}$ compounds (see Figs. 2 and 3) where they also gave excellent results. In this way the Mooser–Pearson diagrams have taken on lives of their own – valid independently of either classical hard-sphere models or fully rigorous quantum-mechanical calculations, but forming simple and powerful bridges between our intuitive ideas and the mathematically exact (but often computationally unattainable) theory.

The most important development in this subject since my 1977 review [4] is contained in Villars' remarkably complete and logical surveys of the structure and properties of 988 AB, 1011 AB_2, 648 AB_3 and 389 A_3B_5 compounds [8]. This is not the place to reproduce Villars' many excellent results, nor could I equal his succinct, elegant and witty presentation. However, to give the reader an idea of the scope of the problems he has solved, a few more numbers should be quoted.

Villars considers 53 physical properties which generate 182 candidates for coordinates. For the AB phases (for example) 20 structure types, each containing 6 or more representatives, account for more than 90% of the 3916 possible phases. Omitting the noble gases and elements with $Z > 95$ gives nearly 80,000 structural possibilities.

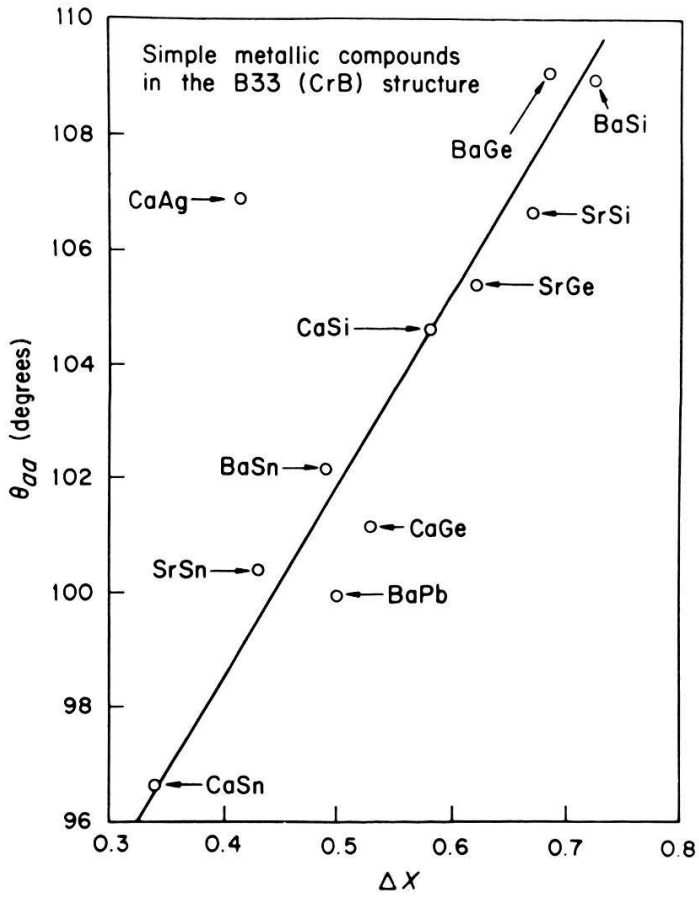


Figure 4
Anion-anion chain (helical pitch) angle θ_{aa} as a function of orbitally (s–p) dependent electronegativity ΔX. Apart from CaAg the linear fit is accurate to about 0.5 degree.

While previous workers had 'chipped away' at constructing structural patterns, Villars now decides to attack this problem using not the best two but the best three coordinates. On the one hand this makes the problem much more difficult since two-dimensional plots are easily constructed graphically and inspected visually. On the other hand, most previous workers omitted the electron/atom ratio from their structural plots. This is a coordinate which has long been employed by metallurgists. The question has always been whether this coordinate enjoys equal status with other coordinates (such as size and electronegativity), or whether it is simply the most convenient (or lazy man's) coordinate.

To answer this question objectively Villars treats all 182 coordinate candidates equally in an ingenious reduction procedure which successfully identifies three types of coordinates for structural plots. How did he avoid constructing three-dimensional plots and how did he make his decisions? The answers to these questions are contained in Villars' beautiful paper [8] but I give the reader a clue: sammelbecken (technically a basin or reservoir, but literally a collection plate).

Two of the three coordinates ultimately obtained by Villars from his statistical analysis are quite familiar. The first is the electron/atom ratio. This concerns the weight of the s–p relative to the d bonds. The second is the electronegativity difference ΔX_{AB}, which determines the total ionic or charge-transfer contribution to the intermetallic bond.

The third coordinate which emerges from Villars' analysis is not traditionally known to crystallographers and metallurgists. It is the A–B difference of the average of the s–p quantum core radii [5, 7]. It appears that this coordinate measures the strongly directional or covalent part of the charge-transfer energy. (Note that this is the coordinate which is used as the abscissa in Fig. 4) The recognition that the charge-transfer energy can be separated into s–p and d parts by using this coordinate represents a major advance in our understanding of intermetallic interaction energies.

Villars' analysis contains many valuable positive results but the negative results are just as useful. For example, he has not only shown that the average of the core s–p quantum radii [5, 7] is a good coordinate, but also that the *classical* hard-sphere atomic radii, whether they are metallic, ionic, or covalent, are *not* good coordinates. Indeed the literature is crowded with empirical structural correlations with many coordinates or physical properties, and Villars shows that almost all (I would guess more than 95%) of these correlations are unsound. It might even be said that Villars' negative results are more valuable than his positive ones. After his papers the phenomenology of materials science will never again be the same.

Among Villars' many interesting results there is one that I can discuss here. Of the 20 AB structure types only one, the NiAs with 23 representatives, was not separated satisfactorily. Nineteen AB structure types with 998 representatives were separated with 97.8% success. Villars concludes that his analysis is not valid for the NiAs structure, whose 23 representatives were scattered all over his diagram. One might explain this result by saying that the NiAs structure is p–d and complex, but there are many other p–d complex structures (such as CrB) among the 19 types treated successfully. It seems to me that Villars' result suggests an endemic structural peculiarity in the NiAs family, which could possibly be a large and intrinsic concentration A of antisite defects [9]. (In

Landau language this would mean $\partial^2 G/\partial A^2 < 0$ at $A = 0$, where G is the free energy.) It is not easy to test this conjecture with diffraction techniques, but if the concentration is large enough it could be found by Mössbauer spectroscopy. Incidentally, such a large native concentration of antisite defects would correspond to a structural analogue of self-stabilized dilute random antiferromagnet or 'spin glass.' The structure actually may be stabilized by the antisite disorder, which would explain the wide scatter of its representatives in a structural plot.

It would seem that Villars' work [8] brings the chapter of science begun by Mooser and Pearson [1] to a conclusion. However, within each structural family there still exist many problems (similar to that shown in Fig. 4 for the CrB family) to be solved. I would prefer to say that Villars has completed one chapter, but his work may well prove to be the beginning of many other chapters. What these may be remains to be seen, but such is the richness of materials science that we can be certain that many interesting and beautiful ideas remain to be discovered.

REFERENCES

[1] E. Mooser and W. B. Pearson, Acta Cryst. *12*, 1015 (1959).
[2] J. C. Phillips, IN *Treatise on Solid State Chemistry*, (Ed. N. B. Hannay, Plenum, New York, 1976), Vol. 1, p. 1.
[3] J. C. Phillips, Phys. Rev. Lett. *20*, 550 (1968); J. C. Phillips, and J. A. Van Vechten, Phys. Rev. Lett. *22*, 705 (1969); J. C. Phillips, Rev. Mod. Phys., *42*, 317 (1970).
[4] J. C. Phillips, Festkörperprobleme *17*, 109 (1979).
[5] J. St. John and A. N. Bloch, Phys. Rev. Lett. *33*, 1095 (1974).
[6] W. Reiger and E. Parthé, Acta. Cryst. *22*, 919 (1967).
[7] J. R. Chelikowsky and J. C. Phillips, Phys. Rev. *B17*, 2453 (1978).
[8] P. Villars, J. Less-Com. Met. *92*, 215 (1983); *99*, 33 (1984).
[9] A. Kjekshus and W. B. Pearson, Prog. Sol. State Chem. *1*, 83 (1964), stress that the NiAs structure is actually found for wide ranges of homogeneity, but the stoichiometric compositions tend to have the NiAs structure in equilibrium only at high temperatures. This is what one would expect from a structure intrinsically stabilized either by antisite defects or vacancies.