the Institut für Strahlen- und Kernphysik der Universität Bonn, Bonn, Germany.

[1] E. N. Kaufmann, P. Raghavan, R. S. Raghavan, E. J. Ansaldo, and R. A. Naumann, Phys. Rev. Lett. 34, 1558 (1975).

[2] E. N. Kaufmann, K. Krien, J. C. Soares, and K. Freitag, Hyperfine Interactions 1, 485 (1976).

[3] E. N. Kaufmann, Bull. Am. Phys. Soc. 21, 407 (1976); and E. N. Kaufman and R. Vianden, Bull. Am. Phys. Soc. 22, 467 (1977).

[4] K. Krien, J. C. Soares, K. Freitag, R. Tischler, G. N. Rao, H. G. Müller, E. N. Kaufmann, A. Hanser, and B. Feuer, Phys. Rev. B 14, 4782 (1976).

[5] E. N. Kaufmann and R. Vianden, to be published.

[6] K. Krien, private communication.

[7] F. A. Shunk, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1969), 2nd Suppl., p. 64.

[8] Ref. 7, p. 116; and M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), p. 292.

[9] Obtained from Franklin Institute Research Laboratories, Philadelphia, Pennsylvania.

[10] On the pre-annealed sample additional surface impurites detected were C, O, F, Si, and Ni. A bulk Ni impurity at the 20-ppm level was also evident. After annealing, the C, Si, and Ni showed evidence of some diffusion into the bulk and the oxide on the surface was more prominent. Scattering from diffused C and Si showed no dependence on crystal orientation, whereas diffused Ni was found to be completely substitutional.

[11] Analytical descriptions of channeling, such as used in Ref. 2, which ignore thermal lattice vibrations are least accurate for that fraction of channeled ions which closely approach atomic rows and planes. The analytical approach also assumes statistical equilibrium in the channeled particle flux which is not acheived experimentally in the near surface region on Be where the Os impurity resides. This has been verified by observation that the degree of narrowing of the Os dip for axial scans depends on the tilting plane chosen through the axis.

[12] M. L. Swanson, F. Maury, and A. F. Quenneville, in *Applications of Ion Beams to Metals*, edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum, New York, 1974), p. 292; L. M. Howe and M. L. Swanson, in *Application of Ion Beams to Materials 1975*, edited by G. Carter, J. S. Colligon, and W. A. Grant (Institute of Physics, London, 1976), p. 273; and references therein.

[13] D. Schumacher, in *Vacancies and Interstitials in Metals*, edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970), p. 910.

[14] H. J. Lipkin, Ann. Phys. (N.Y.) 23, 28 (1963); and P. G. Dawber and R. J.Elliott, Proc. Roy. Soc. London, Ser. A 273, 222 (1963).

[15] C. Janot, P. Delcroix, and M. Piecuch, Phys. Rev. B 10, 2661 (1974).

[16] K. Nishiyama, F. Dimmling, Th. Kornrumpf, and D. Riegel, Phys. Rev. Lett. 37, 357 (1976).

[17] *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972), 3rd ed., pp. 4–115.

[18] A. Hasegawa, B. Bremicker, and J. Kübler, Z. Phys. B22, 231 (1975); and M. Weger and I. B. Goldberg, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, pp. 1–177.

Structural Stability of Suboctet Simple Binary Compounds

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There are forty-five simple binary suboctet non–transition-metal compounds $A^N B^{P-N}$ ($3 \leq P \leq 6$) which crystallize in six crystal structures belonging to two broad families. We show that although these structures cannot be differentiated using isotropic atomic coordinates, successful topological separation is achieved using anisotropic bond-charge coordinates with σ and π symmetry. Anisotropic bond-charge coordinates were previously used by St. John and Bloch to separate the five structures of 59 compounds of the prototypical $A^N B^{8-N}$ octet family.

The prediction of crystal structures has long been considered a difficult problem. The differences in energy between competing structures are of order 0.1 eV/atom, while in general quantum-mechanical calculations of cohesive energies are accurate only to 1 eV/atom (or more), even when use is made of the largest computers. Moreover, the number of possibilities is very large. With $\sim 10^2$ elements and more than 200 space groups, the number of possible combinations of simple binary compounds AB in different structures is of order 10^{10^4}.

The problem of predicting crystal structures may be made more tractable by confining it to observed stable compounds and by grouping compounds into homologous families with the aid of the periodic table. An example of such a chemically homologous family is simple binary non-transition-metal compounds $A^N B^{8-N}$, the "octet compounds," with eight s-p valence electrons per formula unit. There are about eighty such compounds, which crystallize in five different structures. Even in this case there are more than 10^{50} combinations of compounds and structures.

Progress on this problem requires reformation. One must replace prediction of structural energy differences by classification of different structures in a schematic coordinate space. This was first done for intermetallic-alloy solubilities at small concentrations by Darken and Gurry,[1] who were partially (75%) successful using entirely classical atomic size and charge-transfer coordinates (more specifically, Goldschmit-Pauling-Zachariasen atomic radii and Pauling electronegativities). However, the first major breakthrough in classification of crystal structures was made by Mooser and Pearson.[2] They restricted their attention to simple binary compounds AB. Their coordinates were Pauling electronegativity differences (a classical variable based on heats of formation) and the semiclassical average principal quantum number $\bar{n} = \frac{1}{2}(n_A + n_B)$. With these coordinates they were 90–95% successful in separating fourfold- and sixfold-coordinated octet compounds (10^{25} combinations). They were also successful in separating many TB compounds (where T is a transition metal and B^N is a nontransition metalloid with $3 \leq N \leq 5$). An exact quantum treatment of the 4–6 coordination separation of the octet compounds was given by Phillips and Van Vechten[3] using the dielectric method, but their method is restricted to fully bonded cubic structures with no lone pairs.

In this Letter we report an exact classification of fractionally bonded suboctet non–transition-metal compounds $A^N B^{P-N}$ with $3 \leq P \leq 6$. We consider forty-five compounds which belong to two broadly different structural types: twenty-three metallic structures derived from "bcc" CsCl structures and twenty-two anion valence coordination structures (open and solid symbols, respectively). The former belong to the crystal classes $B2$ ($cP2$), $L1_0$ (tP_4), and $B32$ ($cF16$); the $B2$ and $B32$ structures are compared by Pearson[4] (Ref. 4, p. 572). The valence coordination compounds form in the anion zigzag chain (cf. Se and Te) $B33$ ($oC8$) structure, with $P-2N = N_b/N_a = 2$ anion-anion bonds per anion, and anion (perfect, $tI64$, and imperfect, $cP64$) tetrahedral clusters with $P-2N=3$. Both $L1_0$ (tP_4) and $cP64$ can be considered as distorted-boundary phases, just as wurtzite is a distorted-boundary phase for octet compounds.

We first attempted to classify the suboctet $A^N B^{P-N}$ compounds using the semiclassical Mooser-Pearson coordinates. The results are shown in Fig. 1. Because of the digital character of the Mooser-Pearson coordinates eight compounds occupy joint sites, and five compounds violate the optimal domain separation. The classification is generally unsuccessful, with overlap between the two broad classes of bcc structures (open symbols) and anion valence structures (solid symbols). The fine structure associated with the three different classes is not resolved.

The unsuccessful attempt in Fig. 1 led us to utilize the orbitally dependent radii r_l of Simons and Bloch,[5]

$$r_l = \hat{l}(\hat{l}+1)/Z\,, \tag{1}$$

which are the classical turning points of the nonintegral angular momentum $\hat{l}$ determined from free-ion term values E_{nl} by the Fues relation:

$$E(n,l) = -\tfrac{1}{2}Z^2\{n+\hat{l}-l\}^{-2}\,. \tag{2}$$

For the simple binary octet compounds $A^N B^{8-N}$, St. John and Bloch showed[6] that a successful classification resulted, using the coordinates

$$r_\pi = r_\pi{}^A + r_\pi{}^B\,, \quad r_\sigma = r_\sigma{}^A - r_\sigma{}^B\,, \tag{3}$$

where $r_\pi{}^\alpha = r_1{}^\alpha - r_0{}^\alpha$ and $r_\sigma{}^\alpha = r_1{}^\alpha + r_0{}^\alpha$. The coordinates r_π and r_σ correspond to $\bar{n}$ and ΔX (Mooser-Pearson) or E and C (Phillips–Van Vechten), respectively, but are more precise because of their orbital content.

Figure 2 shows that the Simons-Bloch-St. John map successfully separates not only the two broad classes but also the six crystal structures as well, including the two distorted-boundary phases. There is a small circle of confusion just below the $L1_0$ ($tP4$) phase which is not successfully resolved with these coordinates. A successful separation in this neighborhood only can be achieved with normalized coordinates $r_l{}^\alpha/r_{12}{}^\alpha$, where r_{12} is the standard close-packed atomic radius.[7]

There are a number of interesting conclusions which can be drawn from these results. Most important is that the St. John-Bloch coordinates[6] are equally successful for $A^N B^{P-N}$ with $P=8$ and $P \sim 4$. This suggests that these are the proper co-

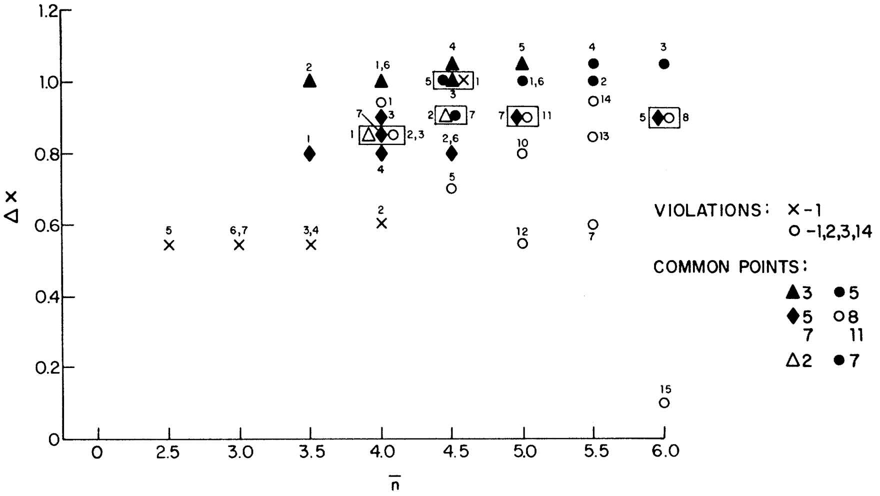

FIG. 1. Mooser-Pearson plot of electronegativity difference, Δx, vs average principal quantum number, $\bar{n}=\frac{1}{2}(n_A+n_B)$. Crosses, (1) NaTl, (2) NaIn, (3) LiIn, (4) LiCd, (5) LiAl, (6) LiGa, and (7) LiZn; open circles, (1) LiTl, (2) LiHg, (3) LiPb, (4) MgHg, (5) MgTl, (6) BaZn, (7) BaCd, (8) BaHg, (9) CaCd, (10) CaHg, (11) CaTl, (12) SrCd, (13) SrHg, (14) SrTl, (15) BiTl, and (16) CaIn; open triangles, (1) LiBi and (2) NaBi; solid diamonds, (1) CaSi, (2) CaSn, (3) SrSi, (4) CaGe, (5) BaPb, (6) SrGe, and (7) SrSn; solid circles, (1) KPb, (2) RbPb, (3) CsPb, (4) CsSn, (5) KSn, (6) RbSn, and (7) NaPb; solid triangles, (1) GeK, (2) KSi, (3) GeRb, (4) CsSi, (5) CsGe, and (6) RbSi.

ordinates for almost all non-transition-metal structures for a wide range of P. Exceptions may be extreme values of P such as $P=2$, where exchange and correlation (the Wigner-Seitz "hole") are especially important; this would explain the usefulness of r_{12} as a normalizing factor in a few cases.

The apparently universal significance of r_σ and r_π as structural parameters for non-transition-metal compounds has important implications for pseudopotential theory. Several recent papers have employed nonlocal pseudopotentials with striking success,[8,9] e.g., in GaAs to *predict*[10] the L_{1c} conduction-band energy with an accuracy of 0.03 eV (compared to the total valence + conduction bandwidth of 20 eV!) or to calculate transi-

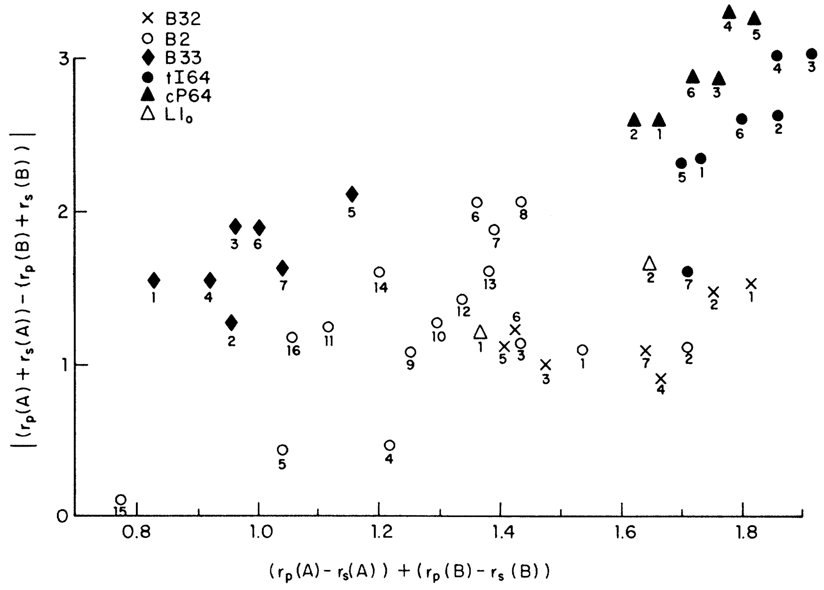

FIG. 2. St. John-Bloch coordinates (Ref. 6). Symbols same as in Fig. 1.

tion-metal surface-state energies self-consistently.[11] The Simons-Bloch radii can be used to reduce greatly the number of adjustable parameters in nonlocal pseudopotentials.[12]

The mathematical interpretation of the elemental coordinates $r_\sigma{}^\alpha$ and $r_\pi{}^\alpha$ is that they correspond to $(s+p)$-hybridized orbitals and $(2p-s-p)$-hybridized orbitals, respectively. (Note that $r_\pi{}^\alpha$ measures the residual strength of π interactions after subtraction of the more stable σ interactions.) A physical interpretation of the bonding coordinates r_σ and r_π can be given in terms of bond charges,[13] which have been shown to play a decisive role in the tetrahedral-octahedral transition of octet compounds.

The fact that r_σ and r_π are powerful structural coordinates suggests that the (lumped) bond charge may be decomposed into σ and π components. Then the signs in Eq. (3) suggest that the π charge is shared (+sign) while the σ bond charges are transferred. This could correspond in real space to an effective bond potential between atoms A and B which has a triple camelback structure. The π-bond charge would be associated with the central well, while the two wells near the effective σ turning points $r_\sigma{}^{A,B}$ competed for the σ charge. All of these effects are small and are superimposed on the nonbonding charge density which, to lowest order, is simply a superposition of atomic charge densities. However, it would appear that these small effects are the ones responsible for structural phase transitions.

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[1] L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill, New York, 1953), pp. 87ff; J. T. Waber, K. Gschneider, Jr., A. C. Larson, and M. Y. Prince, Trans. Metal. Soc. AIME 227, 717 (1963).

[2] E. Mooser and W. B. Pearson, Acta Crystallogr. 12, 1015 (1959), and in *Progress in Semiconductors*, edited by A. F. Gibson, F. A. Kroger, and R. E. Burgess (Wiley, New York, 1960), p. 103. See also W. B. Pearson, *Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1972), pp. 246ff.

[3] J. C. Phillips and J. A. Van Vechten, Phys. Rev. B 2, 2147 (1970).

[4] Pearson, Ref. 2, especially pp. 568ff, 376ff, and 214ff.

[5] G. Simons and A. N. Bloch, Phys. Rev. B 7, 2754 (1973); A. N. Bloch and G. Simons, J. Am. Chem. Soc. 94, 8611 (1972).

[6] J. St. John and A. N. Bloch, Phys. Rev. Lett. 33, 1095 (1974).

[7] L. Pauling, *Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, New York, 1960), 3rd ed.

[8] K. C. Pandey and J. C. Phillips, Phys. Rev. B 9, 1552 (1974).

[9] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 14, 556 (1976).

[10] D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. 37, 766 (1976).

[11] S. G. Louie, K.-M. Ho, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. Lett. 37, 1288 (1976).

[12] J. C. Phillips, to be published.

[13] M. L. Cohen, Science 179, 1189 (1973).

Measurement of Kapitza Resistance by Use of Transient Temperature Response

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We show that the transient temperature response of a freely suspended sample to heat impulses and to heat pulses of varying duration may be interpreted to yield values of the thermal-boundary (Kapitza) resistance to heat flow into He I and He II. Our results show that in He II the thermal flux is carried by first and second sound, each of which has a characteristic Kapitza resistance.

We have developed a new heat-pulse technique for investigation of thermal-boundary (Kapitza) resistance in both He I and He II, which yields evidence for the contributions of first and second sound to the thermal flux in He II.[1,2] Accurate measurements can be made in He I since the data do not require the large corrections which limit the usefulness of conventional steady-state cell measurements.[3]

The injection of a heat pulse into a test body immersed in liquid helium produces a transient temperature response at a point on the surface of the test body. Analysis of this transient provides a direct measurement of the thermal radiative, or Kapitza, relaxation time, $\tau_K = R_K C_A$, where C_A is the sample heat capacity per unit area and