

## Structural Stability of Crystalline Compounds

Global surveys of material properties have attracted much interest in recent years. The problem which has been analyzed in most detail is the mapping of crystal structures of simple binary  $AB$  compounds using phenomenological coordinates.<sup>1-5</sup> On the other hand, an interesting microscopic model of the complex family  $A = (d \text{ transition metal})$ ,  $B = (p \text{ nontransition metal})$  (containing about 200 compounds), which successfully separates crystal structures, has recently been presented<sup>6</sup> in this journal by Pettifor and Podlucky (PP). Excluded from their discussion are compounds where  $B = \text{first-period or } s \text{ metal}$ .

The relative merits of microscopic and phenomenological global surveys are to some extent a matter of taste. Because of the small energy differences between crystal structures one might believe that a tight-binding framework such as that used by PP, which cannot predict equilibrium volumes accurately, would not adequately predict structural energy differences. One instead would expect that self-consistent calculations using a convergent basis set would be necessary.<sup>7</sup> Nevertheless, PP argue that for  $p-d$  compounds the  $p$  and  $d$  atom core repulsive interactions are qualitatively different. This difference, supported by parametrized band energies, explains most of the observed structural patterns.

The progress made recently by the phenomenological approach is not addressed by PP. Villars has recently shown<sup>8</sup> that for all  $AB$ ,  $AB_2$ ,  $AB_3$ , and  $A_3B_5$  compounds (about 3000 in all), 98% successful structural separations are achieved with three coordinates. Two of these are conventional, the electron/atom ratio and electronegativity. The third is unexpected, because the usual atomic size is replaced by the  $s-p$  orbital radii which are based on atomic energies and are not adjustable parameters.<sup>3-5</sup> These radii apparently describe  $s$ ,  $p$ , and  $d$  interactions with an accuracy comparable to that of the instructive but more restricted PP model. Structural diagrams using orbital radii have become important aids in the systematization and correction of structural bibliographies now in preparation.<sup>9</sup>

Statistically, the success of each of these schemes in separating crystal structures is comparable with the probable accuracy of the experimental data. Therefore, the eventual scheme of choice will be determined not only by statistical criteria, but also by its susceptibility to direct physical interpretation and its utility in predicting material properties other than structure.<sup>3-5</sup> Examination of the PP approach from this point of view may prove illuminating.

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