

## Phenomenology of the Crystal Structures of Transition-Metal-Atom Binary Compounds

One of the most successful approaches to the phenomenology of binary  $AB$  systems has been the description of various observables  $S_{AB}^{\text{obs}}(Z_A, Z_B)$  in terms of a function  $S_{AB}(R_1^{AB}, R_2^{AB})$  of a linear dual coordinate system  $R_1^{AB} = |f(Z_A, N_A) - f(Z_B, N_B)|$  and  $R_2^{AB} = g(Z_A, N_A) + g(Z_B, N_B)$ . Here  $Z_\alpha$  and  $N_\alpha$  are, respectively, the atomic number and the number of all ( $s, p, d$ ) valence electrons of atom  $\alpha$ , and  $f_\alpha$  and  $g_\alpha$  are some suitably chosen elementary *atomic* scales (electronegativity, ionic radii, orbital radii,<sup>1</sup> etc.). Common to all such approaches is the recognition that since  $S_{AB}^{\text{obs}}(Z_A, Z_B)$  mirrors the two-dimensional structure of the periodic table,  $f_\alpha$  and  $g_\alpha$  should contain variations both in rows and columns of the periodic table. Recently, Machlin and Loh<sup>2</sup> (ML) have suggested that *atomic-number-independent* elementary scales  $f_A = N_A$  and  $g_A = N_A/2$  (i.e., constant within columns) can be used to predict the crystal structures of the 91 inter-transition-metal-atom (TM) binary compounds (i.e., 16% of the total data base<sup>1</sup>). I comment here on an elementary flaw in ML's work.

Since in the ML approach  $R_1^{AB}$  and  $R_2^{AB}$  do not depend on  $Z_A, Z_B$  (viz. core size and structure) but only on the column numbers  $N_A$  and  $N_B$ , the model predicts that all  $n_i^A n_j^B$  compounds formed between an atom  $A$  from column  $i$  and an atom  $B$  from column  $j$  (a maximum of 9 for TM-TM compounds) will have an identical crystal structure. In their plot,<sup>2</sup> however, these equivalent  $n_i^A n_j^B$  points which should correspond to a single  $(R_1^{AB}, R_2^{AB})$  value were "slightly displaced ... for the sake of clarity."<sup>2</sup> It is easy to see that their reported structural separation depends almost entirely on this arbitrary displacement. This is seen in the lower half of Fig. 1 which depicts the observed crystal structure of 95 TM-TM compounds<sup>3</sup> as a matrix  $S(N_A, N_B)$ . If the ML notion is correct, all crystal structures appearing in any of the  $3 \times 3$  squares (constant  $R_1^{AB}, R_2^{AB}$ ) should be identical. Shading each square for which this condition is not met, one clearly observes that the number of unsuccessful predictions (total shaded area) is overwhelming. This predictive power, approximately equal to a random guess, becomes even worse if only the number of  $d$  electrons  $N_\alpha^d$  is used (upper half of Fig. 1), or if compounds between a TM and a simple atom are considered (20% reliability of the mod-

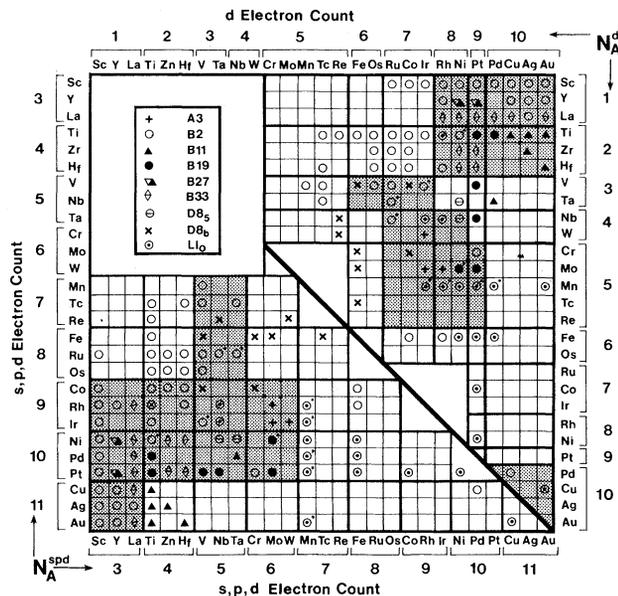


FIG. 1. The observed structural matrix  $S_{AB}^{\text{obs}}(N_A, N_B)$  for TM-TM binary compounds.

el). This proves not only that ML's particular choice of  $f$  and  $g$  is poor, but that *any* choice based on the number of valence electrons  $N$  alone cannot do better. It was previously noted<sup>1</sup> that a successful scale for  $f$  and  $g$  should incorporate (i) variations in columns; (ii) for the subset of TM-TM binaries, a specialized scale including directly also  $d$  coordinates; and (iii)  $s-p$  coordinates. A new, corrected TM-TM scale<sup>4</sup> by ML now introduces features (i) and (ii) explicitly and builds in feature (iii) through the use of bulk band structure parameters from a fully hybridized  $s-p-d$  conduction band. The improved structural separation substantiates points (i)-(iii) but does not isolate any evidence on the role of  $d$  coordinates.

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<sup>1</sup>A. Zunger, Phys. Rev. Lett. **44**, 582 (1980), and Phys. Rev. B **22**, 5839 (1980).

<sup>2</sup>E. S. Machlin and Beiliang Loh, Phys. Rev. Lett. **45**, 1642 (1980).

<sup>3</sup>AuLa has been recently determined to have a B33 structure [O. D. McMaster and K. A. Gschneider, J. Less. Common Met. **25**, 135 (1970)], not the B2 structure (Ref. 2).

<sup>4</sup>E. S. Machlin and Beiliang Loh, following Response [Phys. Rev. Lett. **47**, 1087 (1981)].