

Phillips J. C. Ionicity of the chemical bond in crystals.
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[Bell Telephone Laboratories, Murray Hill, NJ]

Chemical trends in bonding in simple binary octet crystals of formula $A^{NB^{8-N}}$ are discussed in terms of a simplified spectroscopic theory based primarily on the bond length and dielectric constant of each compound, which are used to define the ionicity with a proven accuracy of one percent. [The SC® indicates that this paper has been cited over 450 times since 1970.]

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"In 1963 Marvin Cohen and I, at the University of Chicago, had been studying the energy bands of semiconductor crystals and using their fundamental optical absorption spectra to refine the results of quantum mechanical calculations when we realized that our deductive approach left unanswered some of the most important questions, for both the calculations and the experiment showed systematic chemical trends in bonding which were not easily identified in the starting potentials of the separated atoms. Of course, I knew that some of these trends could be described roughly by Linus Pauling's atomic electronegativity parameters, which he defined as the ability of an atom in a bonded state to attract electrons. But other trends depended on atomic size in a way that I could not determine, and many trends depended on *both* size and electronegativity in some unknown way.

"At this time I became quite discouraged about my ability to

formulate these trends quantitatively. I happened to meet C.A. Coulson at a conference and I mentioned the problem to him. Several students and he tried to treat the problem using the Hückel method, but again they encountered serious difficulties in relating isolated atoms to bonded atoms. Then in 1967 while on sabbatical and in a mood to take larger views, I came to a very simple realization, namely, that the chemical trends had to be describable in terms of only a few experimental observables. One of these was obviously the bond length, while the other (and this was the crucial insight) could be the electronic dielectric constant. "Why the electronic dielectric constant? Because in the work on fundamental absorption spectra I had found that by using the fsum rule on optical oscillator strengths, I could relate the electronic dielectric constant to an average energy gap between occupied bonding electronic states and unoccupied antibonding electronic states. This average energy gap contained both covalent and ionic contributions from the potentials of the atoms in a bonded state. In this respect, it represented an unbiased hybrid of both the Pauling and the Coulson-Huckel approaches. But through the f-sum rule, it contained a new and essential third element, namely, the number of bonding electrons per $A^{NB^{8-N}}$ atom pair. For the heavier atom pairs, d-electrons make this number larger than the eight s-p electrons of classical valence theory, and it is this refinement that makes it possible to define ionicity with an accuracy of one percent."