

Reiss H, Fuller C S & Morin F J. Chemical interactions among defects in germanium and silicon. *Bell Sys. Tech. J.* **35**:535-636, 1956.

Electrons and holes in semiconductors are analogous to hydrogen and hydroxyl ions in water and acceptor and donor impurities are the analogs of acids and bases. Many other analog phenomena, e.g., ion pairing, are possible. This paper verifies this concept. [The SCI® indicates that this paper has been cited over 180 times since 1961.]

Howard Reiss
Department of Chemistry
University of California
Los Angeles, CA 90024

June 10, 1979

"When I joined the technical staff of Bell Laboratories in 1952, I knew little about semiconductors. On reading about this subject I translated ideas into the language of the chemist, thus bringing them into my own frame of reference.

"I was struck by the seemingly awkward approach used to calculate the distribution of electrons over a spectrum of energy levels. I realized that where the statistics could be considered classical (or classical for one group of levels while nonclassical for another), the solving of transcendental equations could be avoided because the distribution of electrons was determined by the chemist's law of 'mass action.'

"Unschooling in solid state physics, I was unaware of the brilliant work of Shottky and Wagner in which defects within crystals (including electrons and holes) were treated as chemical-like entities subject to the law of mass action.¹ Ignorance allowed me to continue my exploration, resulting in the discovery that the elemental semiconductors, germanium and silicon, were the analogs of water as media for chemical-like reactions. The positive hole was the analog of the hydrogen ion while the negative electron corresponded to the hydroxyl ion. A recombined hole and electron corresponded to water. Donors, ionizing to yield electrons, therefore were bases while acceptors, ionizing holes, were acids. An acceptor in the

semiconductor should increase the solubility of a donor by a process identical with the dissolution of an acid by a base.

"I was fortunate to have the collaboration of Calvin S. Fuller, the inventor of the silicon solar cell, and an ingenious and enthusiastic experimentalist. Using the donor, lithium, Fuller quickly demonstrated the predicted increase of lithium solubility in the presence of an acceptor (boron). By analogy with water, a host of new experiments was suggested. With the collaboration of another outstanding experimentalist, F.J. Morin, we demonstrated the existence of 'ion pairing' between donor and acceptor ions. Ion pairing had a profound effect on electron energy levels and mobility, and on impurity diffusion and solubility. Even the rate of ion pairing was measurable. Theoretical predictions were more precise in semiconductors than in water, and there were more ways to measure phenomena.

"We have to ask why (in view of the earlier work of Shottky and Wagner) these experiments attracted so much attention. Shottky and Wagner concentrated on nonstoichiometric compounds, complex substances, whose characteristic parameters were unmeasured or known with limited accuracy. In contrast the elemental semiconductors were simple and available as good, pure, single crystals. Device physicists had accurately measured the characteristic parameters. What attracted attention to this paper was undeniability of the example, i.e., the perfect operation of the law of mass action applied to entities having no independent existence outside of the crystal, and the satisfying analogy with processes occurring in aqueous solution.

"Because of its high mobility, lithium, as a donor, has found little device application. However, its importance remains, since it provides a model for the behavior of other impurities where predictions of theory are not so easily observed. Furthermore, this work is a good example of the value of an interdisciplinary approach where different (but equally valuable) psychologies of innovation can be used for an assault on the same problem with a result exceeding the sum of those obtainable using each approach separately."

1. Wagner C & Schottky W. Theorie der geordneten mischphasen. *Z. Phys. Chem.* (Leipzig) **B11**:163-210. 1930.