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BOOK REVIEW

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Book Review of Zintl Phases: Principles and Recent Developments

Zintl Phases: Principles and Recent Developments. Edited by Thomas F. Fässler (Technical University Münich, Germany). From the series, Structure and Bonding, 139. Edited by D. M. P. Mingos. Springer: Heidelberg, Dordrecht, London, New York. 2011. xii + 164 pp. $189.00. ISBN 978-3-642-21149-2.

This volume contains four fairly diverse chapters that concern different aspects of Zintl phases. The first chapter, which is the broadest in subject matter, provides fairly general assessments of and problems inherent to structures, bonding, and stability of Zintl phases, primarily from theoretical viewpoints. The other three deal with specific areas: Zintl phases, the cubic NaTl structure (loosely, stuffed diamond) and its isotypes; the considerable group of *clathrate* phases, fairly rigid polyatomic frameworks stuffed with cations or anions; and the small number of main-group metal hydrides that qualify as Zintl phases. Three of the chapters contain colored figures.

The first chapter, by Miller, Schmidt, Wang, and You, provides a basic introduction to Zintl phases among various electron-counting rules, followed by several different analyses of the bonding in these and problems associated with them. The original and simple classification assumed an ideal charge-transfer—or later, oxidation state—from the cations to the nominal anions, which may be individual atoms, interbonded clusters, or networks with closed, molecule-like bonding shells, a process that implies products with closed valence bands and semiconduction. The authors usefully remind us that, in fact, three competing bonding categories need to be considered: *ionic*, *metallic*, and *covalent* modes, the first two being isotropic, but the last, anisotropic in nature. Effective participation of the cations becomes increasingly important with less electropositive and more electronically and orbitally rich members. Very briefly, the bonding topics considered in some detail include first principle calculations on configurations and energies of realgar-type molecules: Pn_4S_4 and S_4Pn_4 (Pn = N, P, As); the diverse bonding in MgB_2-type (nominally, stuffed graphite) examples, specifically within ternary Eu(A−B) systems for A−B = Zn−Ga, Zn−Ge, Ga−Ge; and NaTl bonding (stuffed diamond).

The second chapter by Evers considers the NaTl and β-brass-type structures of $A^{I}Tr^{III}$ phases (A = Li−Cs, Tr = Al−Tl), including the effects of pressure on stability. The 6 of 40 possibilities that are stable at ambient pressure are expanded to 14 with diamond anvil-cell applications. The results of DFT (WIEN2k) calculations are reported for all 40, evidently for the first time. The writing is detailed, sometimes awkward, but always understandable. About 5% of the references are 10 years old or less.

The third chapter by Shevelkov and Kovnir covers the sizable family of inorganic (nonhydrate) clathrates that may qualify as Zintl clathrates. The frameworks that distinguish members are, in fact, stable only when inner polyhedra are populated with, usually, cations (assuming the likely charge-transfer characteristics, as before) but not with molecules, as in the gas hydrates. Examples of the six Zintl clathrate types are well illustrated and discussed, including their general band characteristics and their inverse anion-stuffed counterparts, if any. Experienced views of non-Zintl clathrates are given in terms of cation defects, lattice distortions, and, again, orbital contributions from the cations. Syntheses and thermoelectric considerations are also included.

The fourth, shorter chapter by Häussermann, Kranak, and Puhakainen is a discussion of the field of metal hydrides as Zintl phases. Presently, these contain either discrete or interstitial hydride anions surrounded by fairly electropositive neighbors or hydrogen-bonded directly to a main-group atom in some network, principally built from triel or tetrel atoms (Al, Ga, Si).

The topics discussed fairly match the objectives as defined by the title of the volume. Perhaps the largest portion of Zintl-phase chemistry that is untouched here, and properly so, is the extremely diverse catalog of even more Zintl phases that keep appearing in the literature. These often delight us in their breadth and diversity, sometimes with compositions and structures that would be difficult to imagine or design ahead of time.

These presentations will be valuable to anyone studying not only Zintl phases but also their intermetallic neighbors and related systems. Some aspects of the analyses are widely applicable. The series *Structure and Bonding* is classified as a journal, and chapters can be downloaded through some university library services.

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