

# *Ab initio* calculations of the electronic structure of $\text{Ca}_{14}\text{MnBi}_{11}$ and $\text{Ba}_{14}\text{MnBi}_{11}$

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The zintl phase compounds based on magnetic Mn ions and typified by  $\text{Ca}_{14}\text{MnBi}_{11}$  and  $\text{Ba}_{14}\text{MnBi}_{11}$  show unusual magnetic behavior, but their 104 atoms primitive cell has precluded any previous full electronic structure study. Using an efficient, local orbital based method within the local spin density approximation to study the electronic structure, we find a gap between a bonding valence band complex and an antibonding conduction band continuum. The bonding bands however lack one electron per formula unit of being filled, leading to a characterization of these compounds as low carrier density *p*-type metals. The Mn atom is magnetic with a moment of 4.5-4.6  $\mu_B$ , so the compounds can be pictured as an array of spin  $\frac{5}{2}$  atoms in a covalent-metallic background.  $\text{Ca}_{14}\text{MnBi}_{11}$  is found to be ferromagnetic as observed, while for  $\text{Ba}_{14}\text{MnBi}_{11}$  (which is antiferromagnetic) the ferro- and antiferromagnetic states are calculated to be essentially degenerate. The bonding is discussed in relation to the zintl concept of crystal cohesion, and we also consider the possible origin(s) of magnetic coupling of the Mn spins.