Enriching the Complexity of Intermetallics through Relativistic Elements

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Complexity in the solid-state can emerge structurally or chemically. Complex structures are characterized by the nature of their long-range and short-range order; examples range from crystals with large unit cells to structures with incommensurately modulated periodicity or quasiperiodicity to structurally amorphous solids. Chemical complexity, on the other hand, arises simply by increasing the compositional variables; even simple close packed structures, become challenging to characterize when multi-component systems are explored and disorder sets in. Intermetallic compounds can be particularly of complex because of their diverse bonding features, stunning structural variations, and exceptional breadth of physical properties. They also have widespread application for construction materials, catalysts, magnets, high performance alloys for energy storage and conversion, as well as for other highly specialized applications.

We have explored and developed a growing number of new families of intermetallic compounds, discovering chemistry well beyond classical valence electron counting rules, such as the Zintl-Klemm (octet) or Hume-Rothery schemes. A recent strategy to attain a greater variety of new compositions, structures, and enhanced stabilities has been achieved by including a late transition metal into the binary active metal–triel. Pd, Pt, Ag, and Au have been especially effective, and Au has a 'magic' effect, giving much new chemistry, arising from its enhanced electronegativity and filled $5d$ orbitals. By way of relativistic effects, Au and Pt exhibit absolute electronegativities on par with I, Se, and Te. Also, since they have fewer valence s and p electrons, Au and Pt offer

Fig. 2. The first Na-containing Bergman-type icosahedral quasicrystal.

interesting bonding modes with active metals by being electron-acceptors as well as showing significant back donation from their filled $5d$ orbitals. Synthetic efforts were exceptionally fruitful for alkali metal-Au-Group 13 or 14 and alkaline earth-Pt-Cd phase spaces. The most significant outcomes occurred during systematic investigation of the Na-Au-Ga system, which yielded various Bergman-type and other crystalline approximants (ACs) of icosahedral and decagonal quasicrystals (QCs). $Na_8Au_{9.8}Ga_{7.2}$ is a rare representative of a decagonal AC not containing Zn or Al (Fig. 1). We demonstrated the critical role of d orbitals in the formation of Bergman-type QCs and ACs, and identified the first Na-containing icosahedral
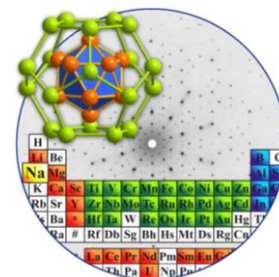
QC in the Na-Au-Ga outcomes from Na-Au-(Ga, consistent and higher order, results that underlying Hume-Rothery-Explorations of the electron also involving the heavier uncovered numerous new feature large coordination alkali metals together with Electronic structure

Fig. 1. (Au/Ga)$_7$ clusters in the decagonal approximant Na$_8$Au$_{9.8}$Ga$_{7.2}$.

system (Fig. 2). Other fruitful Ge, Sn) systems are cubic ACs with unprecedented structural models of shed new insights about the type mechanisms for their stability. poorer parts of the *A*-Au-Ga systems alkali metals K, Rb, and Cs polar intermetallic phases, which polyhedra surrounding the larger complex Au-heteroatom networks. calculations show optimized polar-

covalent bonding within the Au-heteroatom networks as well as empty *d*-filled *d* orbital interactions involving the heavy alkali me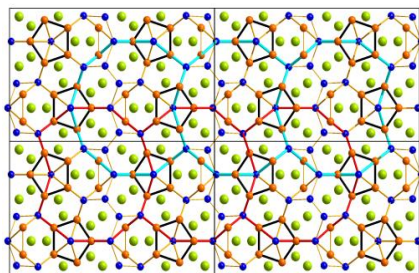tal and Au as an additional stabilizing mechanism.