Chemical Driving Forces and Pathways for Incommensurability in Intermetallic Phases

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Intermetallic phases exhibit a vast structural chemistry, much of which can be rationalized in terms of simple structures being fragmented, rearranged, distorted, and—in some cases—modulated in an incommensurate fashion. Building a predictive understanding of how modulations emerge in these compounds is made challenging by the need for models for how their structures, bonding, and compositions are related. In this presentation, we will discuss theoretical approaches that have been developed in our group to visualize the factors shaping intermetallic structures, and see how they can be applied to guiding new experimental investigations and identifying scenarios where incommensurate order may arise. One of these approaches, the reversed approximation Molecular Orbital (raMO) method, uses the occupied crystal orbitals of a compound to build local bonding schemes, allowing us to trace electron counting rules to closed shell configurations associated with specific geometrical motifs. As we will show for the Nowotny Chimney Ladder (NCL) phases[1] and the incommensurately modulated structure of $Co_3Al_4Si_2$,[2] such bonding schemes can set up situations in which the removal or insertion of fractions of atoms per unit cell can tune the Fermi energy to a pseudogap or band gap, setting the stage for modulations. Another method, the DFT-Chemical Pressure (DFT-CP) analysis, highlights the local interatomic pressures that can emerge in dense atomic packings due to their inability to simultaneously optimize every interatomic distances. The relief of such local chemical pressures (CPs) underlies a range of structural phenomena, including the insertion of interfaces into simple structures,[3] substitution patterns,[4] and local icosahedral order.[5] In the case of $CaPd_5$, these CPs can also drive the formation of a composite structure.[6] As we discuss these examples of structural chemistry analysed with the raMO and DFT-CP methods, a common theme will emerge: CP quadrupoles, a hallmark of soft atomic motions,[7] can anticipate the paths by which intermetallic phases can respond to issues in their electronic banding filling and intermetallic atomic packing. Networks of atoms exhibiting CP quadrupoles are then expected to be highly susceptible to modulations and phase transitions, leading to strategies for the discovery of new incommensurate phases.

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