

Structure, bonding, and properties of Sc intermetallics with transition metals and gallium

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Excess electrons not needed by the more electronegative component in heteropolar intermetallics create fascinating quantum effects but also unconventional chemical bonds. In this context, scandium-rich intermetallics with transition metals and gallium represent a structurally complex and chemically rich family of compounds yet remain largely underexplored.

The systematic study of the Sc–{Mn, Fe, Co, Ni, Pd, Pt}–Ga systems [1,2] has uncovered a homologous series of Sc-rich ternary compounds, Sc₅₄(M,Ga)₁₇ (M = Mn, Fe, Co, Pd, Pt), crystallizing in the Hf₅₄Os₁₇-type structure (*Immm*). These phases exhibit distinct bonding motifs characterized by electron-rich, multi-center bonding within the Sc-based octahedra, which stack into Mackay-type icosahedral clusters - motifs typically found in quasicrystalline materials. Despite their structural complexity, the Sc₅₄(M,Ga)₁₇ phases exhibit relatively large homogeneity ranges, primarily arising from mutual substitution between the transition metal (M) and gallium. This substitutional flexibility points to a significant degree of site disorder and electronic adaptability that contributes to the stability of the overall framework. It is quite intriguing that the compounds with Mn and Fe exhibit semimetallic behavior.

Despite having a lower Sc content than the Sc₅₄(M,Ga)₁₇ phases, the Sc₅₀Co₁₃Ga₃ compound (ϵ -Mg₂₆Ag₇-type structure, *F-3m*) retains Mackay-type icosahedral clusters. It shows potential for incorporating small electronegative elements (e.g., oxygen) inside the Sc octahedra, where the highest electron localization occurs. Further decreasing the Sc content leads to the disappearance of the Mackay clusters while retaining the original and partially substituted Sc octahedra, as seen in the Sc₆Co_{1.73+x+y}Ga_{1-x} (*Immm*) and Sc₁₀(M,Ga)₄ kappa phases (M = Co, Ni). Notably, the Ni-containing kappa phase exhibits semimetallic properties characterized by an indirect band gap.

The formation of homogeneity regions in both the binary and ternary compounds across these systems and the semimetallic features are explained within the framework of the Hume-Rothery phases.

[1] Romaka, V.V., Rogl, G., Binder, G., Michor, H., Bursik, J., Grytsiv, A., Giester, G., Rogl, P. (2022). *J. Alloys Compd.*, **919**, 165540

[2] Romaka V.V., Rogl G., Bursik J., Grytsiv A., Giester G., Rogl P., (2024). *J. Alloys Compd.*, **998**, 174864

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