Universal origin of anomalies in compressed liquid alkalis

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Abstract

Alkali metals are archetypal nearly-free-electron systems, yet compression drives them away from simple-metal behavior. In the liquid phase pressure induced structural transitions and thermodynamic compressibility anomalies have been reported experimentally in some systems. Independently, computational studies have indicated localization of charge and formation of electride-like states in the liquid. Considering all these phenomena as anomalies in compressed liquid alkalis, we apply first-principles molecular dynamics to liquid Na, K, Rb and Cs under pressure, to form a unified picture of all these phenomena across the alkali series. Specifically, we show that these phenomena are initiated by pressure induced electronic reconfiguration and interstitial electron localization and not just by densification. Compression transfers valence charge from delocalized *s*-like states into *p*-character states in Na and *d*-character states in K, Rb, and Cs, accompanied by the emergence of electride-like interstitial localization before the main structural rearrangement. The liquid structure subsequently opens, with the coordination number decreasing from 13-14 to 8-10, while the sound velocity exhibits a softening anomaly that appears prior to the coordination-number reduction. Furthermore, in K, Rb, and Cs, a quantitative electronic coordinate for the transitions is formulated. These results identify orbital reconfiguration and interstitial electron localization as the microscopic mechanism by which pressure drives both structural and compressibility anomalies in alkali-metal liquids and suggest a general pressure-driven route from simple metallic liquids to complex electride-like states.