Alkali Metals and the Chain-Melted Phase of Matter

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Various single elements form incommensurate crystal structures under pressure, where a zeolite-type "host" sublattice surrounds a "guest" sublattice comprising 1D chains of atoms (fig 1). On "chain melting", diffraction peaks from the guest sublattice vanish, while those from the host remain. Diffusion of the guest atoms is expected to be confined to the channels in the host sublattice, which suggests 1D melting. Here, we present atomistic simulations of Potassium to investigate this phenomenon, and demonstrate that the chain-melted phase has no long-ranged order either along or between the chains. This 3D disorder provides the extensive entropy necessary to make the chain melt a true thermodynamic phase of matter, yet with the unique property that diffusion remains confined to 1D only.

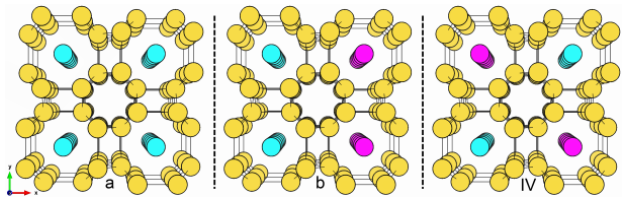
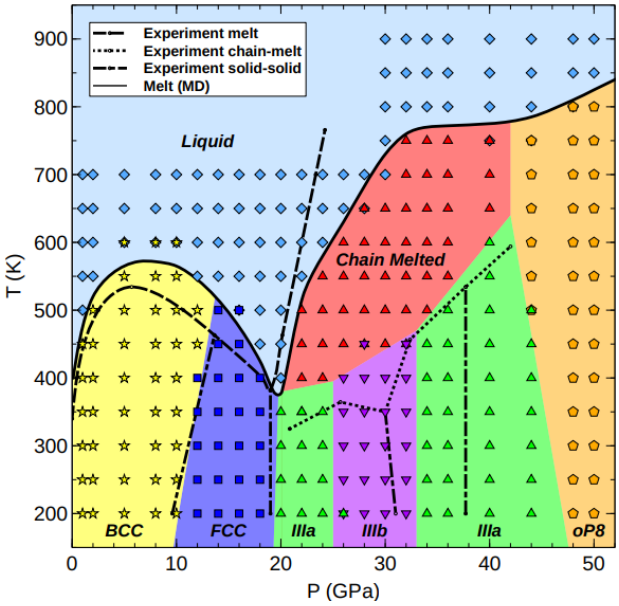


Figure 1. Incommensurate host-guest structure Potassium-III, Yellow (cyan, magenta) spheres denote the host (guest) atoms. Guest symmetries for the IIIa, IIIb, and Rb-IV structures labelled a,b and IV respectively. Chains with the same colour are in-line along the c-axis.

Calculations necessitated the development of an interatomic forcefield using machine learning (MLMD), which we show fully reproduces Potassium's phase diagram (fig 2), including the chain-melted state and 14 known phase transitions. The alkali metals enter complex solid crystal phases with increasing pressure and the liquid is likely to follow with similar nature. Here we investigate the high pressure liquid and transitions around the melting lines in the more massive alkali metals.

Figure 2. Forcefield simulated phase diagram of Potassium. Each datapoint represents an MLMD NVT calculation initialized in the shown phase at 200 K and the corresponding DFT density and then heated. Symbols distinguish the various phases: each simulation was repeated several times, and double-symbols indicate where the final phase was ambiguous.



Colored regions refer to the simulated region of stability for each phase; solid black line is the melting line obtained from the simulations. Chain-melting was determined by the loss of correlation between chains. Experimental phase boundaries for melting (dashed lines), chain-melting (dotted), and solid-solid phase transitions (dash-dotted) are taken from Ref. [1].

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[1] McBride EE, et al. (2015) One-dimensional chain melting in incommensurate potassium. Phys. Rev. B 91(14):144111