Size-effects in Layered Ferrielectric $CuInP_2S_6$

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Transition metal thiophosphate (TMTP) family is a vast chemical space of layered materials incorporating honeycomb or bipartite triangular lattices of metal cations into a flexible framework of $P_2(S/Se)_6^{4-}$ anions. TMTPs exhibit various types of lattice and spin ordered states, naturally tempting to think of these materials as precursors to "ferroelectric graphene" and "ferromagnetic graphene" – 2D or quasi-2D materials, with long-range lattice, magnetic and electronic correlations. [1] In this talk, we will analyze ferroelectric domains in $CuInP_2S_6$.

We have achieved control over ferroelectric T_c in this material via chemical phase separation into locally dielectric $In_{4/3}P_2S_6$ and locally ferroelectric $CuInP_2S_6$. The associated coherency strain increases the T_c up to 340 K from 309K in the bulk [2]. On the other hand, kinetic control of the chemical phase-separation confines chemical phases from several microns to several 10's of nanometers without changing chemical composition. Upon reasonably fast quench, this results in complete, but fully reversible suppression of ferroelectricity at room temperature.

Ferroelectric domains continue to persist as the 2D limit is approached; samples as thin as 10 nm are seen to exhibit polarization, far below the expectations based on Landau-Ginzburg model for a proper ferroelectric semiconductor [3]. Likewise, ferroelectric domains do not follow the conventional Kittel scaling law as a function of thickness. From analytical modeling of the polarization screening, we surmise the existence of an intrinsically doped surface of these materials – echoing a famous hypothesis of 2DEG existing on open ferroelectric surfaces.

Finally, local ferroelectric switching in ultrathin flakes is intertwined with ionic diffusion, where Cu atoms are displaced into the van-der-Waals gap by an electric field. This may result in erratic and damaging switching at room temperature. Owing to much stronger temperature dependence of ionic diffusion, the two phenomena can be decoupled, allowing for more reliable switching [3]. At the same time, ionic-ferroelectric coupling can be potentially exploited to create nanoscale ferroelectrics or even bistable ionic systems that are not themselves ferroelectric.

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