

## Dynamics of some Nano-Ferroelectrics and Multiferroics

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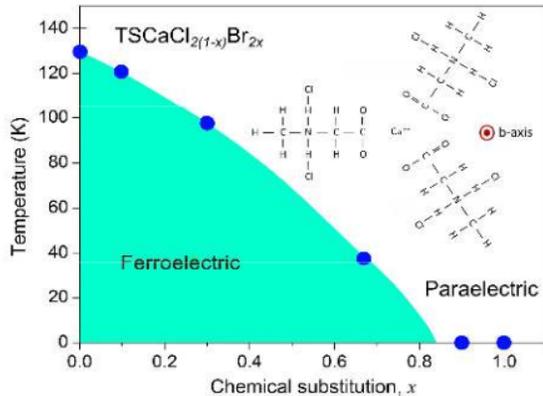
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In this talk I will briefly discuss three experiments for which conventional DFT calculations fail due to the dominance of aperiodic boundary conditions: (1) High-symmetry faceting instabilities in low-symmetry crystals<sup>1</sup> with macroscopic demonstration examples ("toys"); (2) Faceting oscillations due to electrical charging of nano-disks, with a highly accurate simulation<sup>2,3</sup> relating the faceting with internal atomic-scale domain realignment; (3) Cylinder stress in nano-crystals.<sup>4</sup> However most of the talk will be devoted to new work on ferroelectric quantum critical points (QCPs). Very recently we presented<sup>5</sup> studies of the quantum critical point (QCP) in the uniaxial ferroelectric tris-sarcosine calcium bromide, which has critical dimensionality  $d(\text{eff}) = d + z + 1 = 5$ , in contrast to  $d(\text{eff}) = d + z = 4$  in  $\text{SrTiO}_3$  [Fig.1]. We showed that the theoretical prediction of Khmel'nitskii<sup>6</sup> that critical exponent for isothermal susceptibility  $\gamma = 3$  is violated, and that  $\gamma = 2$ , due to ultra-weak polarization (its Curie constant  $C$  is proportional to  $T_c$ , so that both drop to zero at  $T=0$ ).

More recently we extended these studies to  $(\text{Ba,Sr})\text{Fe}_{12}\text{O}_{19}$  (M-type hexaferrite) with data down to 300 mK.<sup>7</sup> This material, unlike  $\text{BiFeO}_3$ , exhibits a strong ferromagnet moment, with ferrimagnetic ordering of its  $\text{Fe}^{+3}$  spins. Unlike other ferroelectric QCPs, it is ferroelectric above its incipient QCP (which like  $\text{SrTiO}_3$  or  $\text{KTaO}_3$  extrapolates to tens of degrees below  $T=0$ ). Due to the fact that the  $(\text{Ba,Sr})\text{Fe}_{12}\text{O}_{19}$  crystal used is quite some distance away from the quantum critical point, neither of these exponents were



observed. We find two unexpected results: (1) below 5K the dependence of dielectric constant  $\epsilon'(T)$  is not monotonic and resembles that in  $\text{SrTiO}_3$  and  $\text{KTaO}_3$ ; we interpret this as arising from coupling of the soft mode to acoustic phonons; (2) the critical exponent  $\gamma$  that describes the divergence of  $\epsilon'(T)$  above 4K describes a power-law dependence with  $\gamma = 1.5 \pm 0.1$ , which differs significantly from both the value 2.0 for quasi-cubic materials with  $d+1 = 4$  and from Khmel'nitskii's theory for anisotropic uniaxial

ferroelectrics with  $d+1 = 5$  and  $\gamma = 3$ . It displays the non-monotonic dip in reciprocal dielectric constant below ca. 5K ("Rowley dip") seen in other QCP systems due to electrostriction. A model for this is presented that is an extension of the phenomenological Barrett Equation, related to work by Tokunaga<sup>8</sup>). We show however that the form of the dielectric function of this quantum paraelectric (it has a fairly large optical gap frequency of  $42 \text{ cm}^{-1}$  at  $q=0$  and at  $T = 6\text{K}$ ) may still be well described by the self-consistent phonon model, even under the approximation of a wavevector-independent soft mode frequency (the Einstein approximation); this involves a carefully justified extension of the Barrett Equation.

Dome-shaped phases in the graphs of  $T$  versus  $X$  in superconductors and magnets, where  $X$  is pressure, or magnetic field, or percentage concentration of some constituent element, are also phenomena of great current interest. Interesting states of matter and unusual physical properties often are often found near these phase boundaries. However, such dome-shaped phases are highly unusual if not unique in  $(T,E)$  phase diagrams in ferroelectrics. Here we look (unsuccessfully!) for the presence of such domes in both lead iron niobate ( $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ) and lead iron tantalate ( $\text{PbFe}_{1/2}\text{Ta}_{1/2}\text{O}_3$ ) mixed into single chemical phase compounds with lead zirconate titanate ( $\text{PbZr}_{0.47}\text{Ti}_{0.53}\text{O}_3$ ) to produce high-temperature magnetoelectric multiferroics (PFNZT and PFTZT). Each dome-shaped phase has been predicted by Glinchuk et al.<sup>9</sup> to exhibit a quantum critical point (QCP) -- a phase transition at  $T=0$  -- at ca. 5% and 20%  $\text{Fe}^{+3}$ -ion B-site occupancy (four QCPs in all in the two materials PFNZT and PFTZT). The experimental data do NOT however reveal dome-shaped phases in the  $T$  vs. %Fe phase diagram, nor any QCPs, but are compared with the general theoretical predictions of Das and others<sup>10-13</sup> and with experiments by Kim et al.<sup>14,15</sup> Finally we note that these  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ -PZT materials are indeed single-phase crystals and not nano-composites; this is proved by the fact that the B-site Fe,Nb,Ti,Zr occupancy ratios are not static but change dynamically with temperature, as shown by the NMR studies of Raevski et al.<sup>16</sup>

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