Physical constraint and its consequence for hyperferroelectrics

Huaxiang Fu
Department of Physics, University of Arkansas, Fayettville, Arkansas 72701, USA

Hyperferroelectricity (HyFE) is a new phenomenon of fundamental importance since hyperferroelectric solids are capable of developing ferroelectricity under an open-circuit boundary condition, despite the existence of strong depolarization fields.[1] Unlike *improper* ferroelectrics (in which the dominating soft mode is nonpolar, and the polarization results from the polar-nonpolar mode coupling),[2–7] HyFEs are *proper* ferroelectrics with a dominating polar instability and a strong polarization.

For decades it has been known that proper ferroelectrics (FE) exhibit ferroelectric phase transition and mono-domain polarization only when the depolarization field is sufficiently screened, e.g., under the short-circuit boundary condition or surrounded by metallic electrodes[8]. When the depolarization field is not screened, FE polarization tends to form multi-domains along the direction of the depolarization field.[9] Another possibility is that proper FEs may undergo a different phase transition by forming vortex.[10] However, the recent discovery showed that HyFE solids defy the accepted belief by being able to retain a mono-domain polarization even under the open-circuit boundary condition,[1] opening a new field of ferroelectric physics[11]. Furthermore, HyFE solids are technologically important since, by forming interface with other functional materials such as semiconductors, strongly-correlated oxides, or multiferroics, the polarization retained in HyFEs can effectively control and/or tune the materials properties across the interface.

However, HyFEs remain mystic, and so far were found only in some uncommon semiconductors LiZnAs, LiBeSb, and LiBeBi.[1] Many key questions of general interest remain to be answered. For example, what is the criterion, if any, that a hyperferroelectric must satisfy? Is there any law governing the magnitude of polarization to be retained by a HyFE under the open-circuit boundary condition? Furthermore, one may wish some intuitive knowledge that may guide the designing of new HyFEs. Obviously the lack of sufficient understanding hampers the searching for other HyFE materials.

In this study, based on a fourth-order Ginzburg-Landau theory[12], we formulate a physical constraint that a HyFE must satisfy. The constraint leads to a nonzero polarization under the open-circuit boundary condition as well as a stable electric state as the minimum of the free energy. The theory further reveals a guide principle on the search for new hyferroelectrics, i.e., they need to have a deep potential well and a small zero-field polarization. In addition, we show that an unstable longitudinal optical phonon is a natural consequence of the constraint. Prototypical ferroelectric $BaTiO_3$, $PbTiO_3$, and $KNbO_3$ do not meet the physical constraint, and are not hyperferroelectrics.

This work was supported by the Office of Naval Research.

[1] K.F. Garrity, K.M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. **112**, 127601 (2014).
[2] C.J. Fennie and K.M. Rabe, Phys. Rev. B **72**, 100103 (2005).
[3] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone, and P. Ghosez, Nature (London) **452**, 732 (2008).
[4] N. Sai, C.J. Fennie, and A.A. Demkov, Phys. Rev. Lett. **102**, 107601 (2009).
[5] N.A. Benedek and C.J. Fennie, Phys. Rev. Lett. **106**, 107204 (2011).
[6] J.M. Rondinelli and C.J. Fennie, Adv. Mater. **24**, 1961 (2012).
[7] M. Stengel, C.J. Fennie, and P. Ghosez, Phys. Rev. B **86**, 094112 (2012).
[8] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).
[9] C. Thompson, D.D. Fong, R.V. Wang, F. Jiang, S.K. Streiffer, K. Latifi, J.A. Eastman, P.H. Fuoss, and G. Stephenson, Appl. Phys. Lett. **93**, 182901 (2008).
[10] I.I. Naumov, L. Bellaiche, and H. Fu, Nature (London) **432**, 737 (2004); I. Naumov and H. Fu, Phys. Rev. Lett. **98**, 077603 (2007).
[11] N.A. Benedek and M. Stengel, Physics **7**, 32 (2014).
[12] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, (Butterworth-Heinemann, Oxford, 2000).