First-principles Determination of Phonons and Related Properties

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Why Phonons?

- Fingerprint of a material: Raman, IR spectra
- Thermodynamic stability: vibrational entropy T, soft modes
- Properties: elastic, dielectric, piezoelectric, etc (couple with fields)
- Structural Transitions: instabilities of a structure $w \rightarrow 0$
- Phonons coupled with electrons, spin, exciton, polarons; e.g. superconductivity

SiC

Ref. Thomas, Pandey and Waghmare, Phys Rev B (Rapid Comm), 77, 121203 (08)

SiC: a promising technological material both as a bulk and at nano-scale

(see a review by Melinon et al, Nature Materials 6, 479 (2007)).

Bulk SiC: mechanical hardness, optical properties (large band gap), bio-compatibility, high-temperature stability, chemical inertness, shock resistant, high refractive index

Stacking (eg. ABCAB...) of crystal planes **(polytypes)** tune properties

1950: Shockley predicted SiC would replace Si

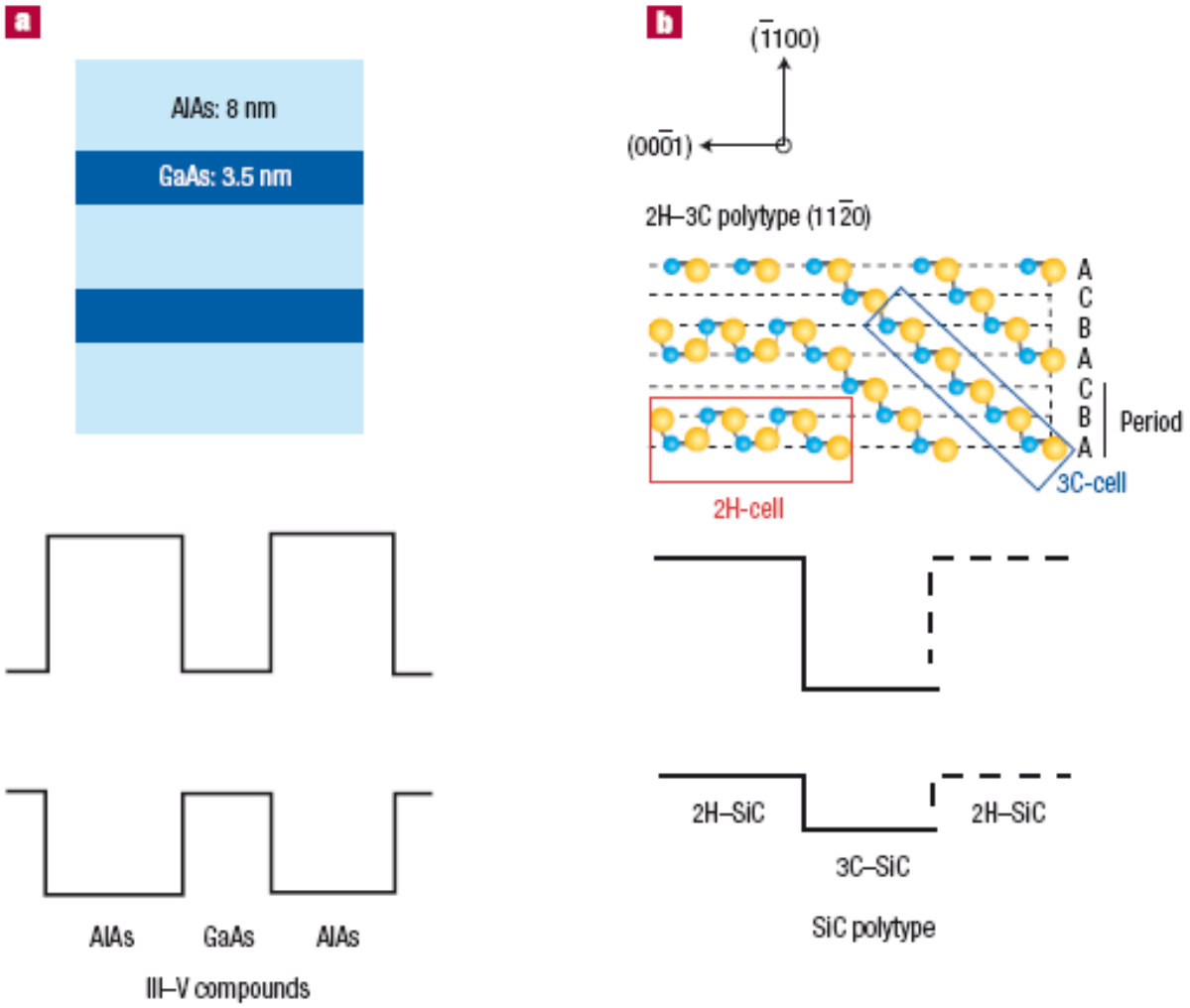
Many applications from power electronics to catalysis

Nano-form of SiC: Atomic engineering of nano-structures to tune properties

Clusters,

Nano-wires, nano-tubes,

Heterostructures



(From Nature Mat. 6, 479 (2007)).

Ultrahigh-quality silicon carbide single crystals

Daisuke Nakamura[1], Itaru Gunjishima[1], Satoshi Yamaguchi[1], Tadashi Ito[1], Atsuto Okamoto[1], Hiroyuki Kondo[2], Shoichi Onda[2] & Kazumasa Takatori[1]

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Silicon carbide (SiC) has a range of useful physical, mechanical and electronic properties that make it a promising material for next-generation electronic devices[1,2]. Careful consideration of the thermal conditions[3–6] in which SiC {0001} is grown has resulted in improvements in crystal diameter and quality: the quantity of macroscopic defects such as hollow core dislocations (micropipes)[7–9], inclusions, small-angle boundaries and long-range lattice warp has been reduced[10,11]. But some macroscopic defects (about 1–10 cm^{-2}) and a large density of elementary dislocations (~10^4 cm^{-2}), such as edge, basal plane and screw dislocations, remain within the crystal, and have so far prevented the realization of high-efficiency, reliable electronic devices in SiC (refs 12–16). Here we report a method, inspired by the dislocation structure of SiC grown perpendicular to the *c*-axis (*a*-face growth)[17], to reduce the number of dislocations in SiC single crystals by two to three orders of magnitude, rendering them virtually dislocation-free. These substrates will promote the development of high-power SiC devices and reduce energy losses of the resulting electrical systems.

Nature 430, 1010 (2004)

Developed a method for making SiC crystals/wafers that have two to three orders of magnitude lower density of dislocations.

Repeated A-Face (RAF) growth:

At each stage, the crystal is carefully rotated so that the solidifying compound crystallises on the best, least-blemished face.

News Report on BBC

Last Updated: Wednesday, 25 August, 2004, 17:28 GMT 18:28 UK

Door open for silicon replacement

A replacement for the use of pure silicon in electronics has come a step closer, the journal Nature reports.
Silicon chips can malfunction at high temperatures, often from the heat generated in their own circuitry.

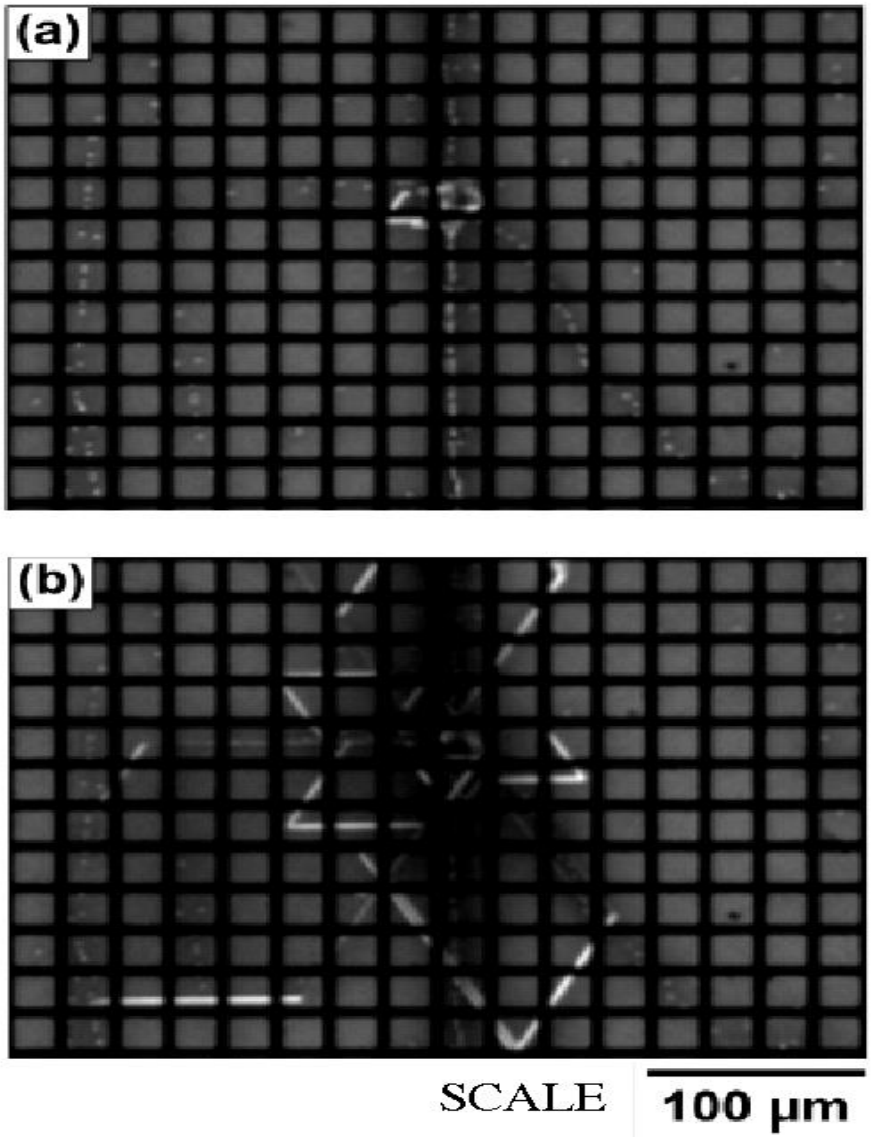
But Japanese experts have now overcome the flaws that plague crystals of silicon carbide, a hard compound that is more robust in hot conditions.

This material could now fulfil its potential as a replacement for pure silicon in manufacturing processes. Silicon carbide (SiC) could be used to make electronic devices that can operate at high power, in fierce heat or at lethal doses of radiation.

If the breakthrough can be carried forward commercially, it could spawn a wide range of improved devices, including electronics that work in red-hot jet engines, better wireless communications and radar, as well as improving smart devices that optimise performance in cars.

Problem: Stacking fault expansion in SiC

Ha, Skowronski, Sumakeris, Paisley and Das, Phy. Rev. Lett. 92, 175504 (2004)



OEM showing development of rhombic stacking faults in the basal plane of 4H-SiC when used in p-i-n diode

(a) Virgin diode

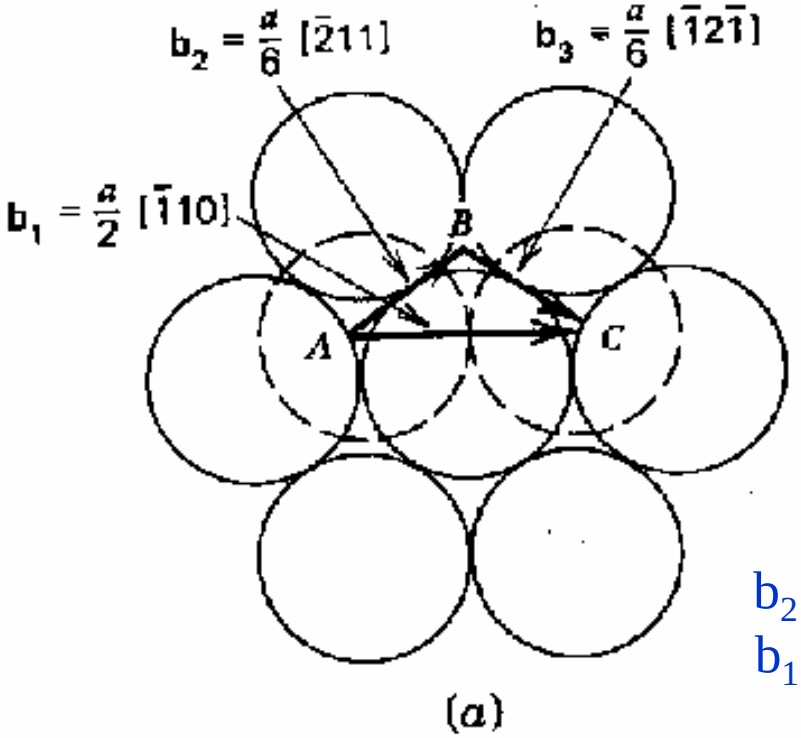
(b) Diode after 5 minutes of biasing at 50 A/cm^2

► Degraded performance: ΔV changes by up to 1 V!

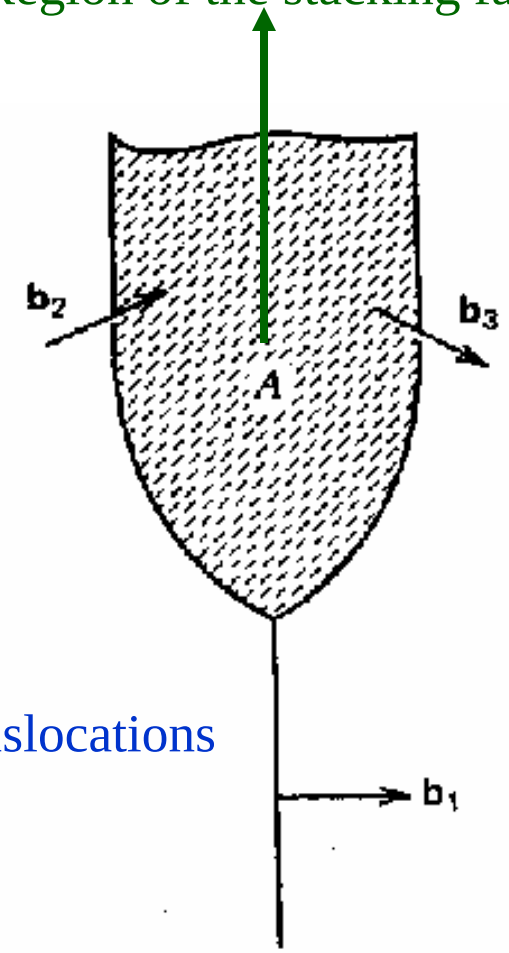
Fundamental Problem

Origin of this phenomenon needs to be understood.

Stacking Faults

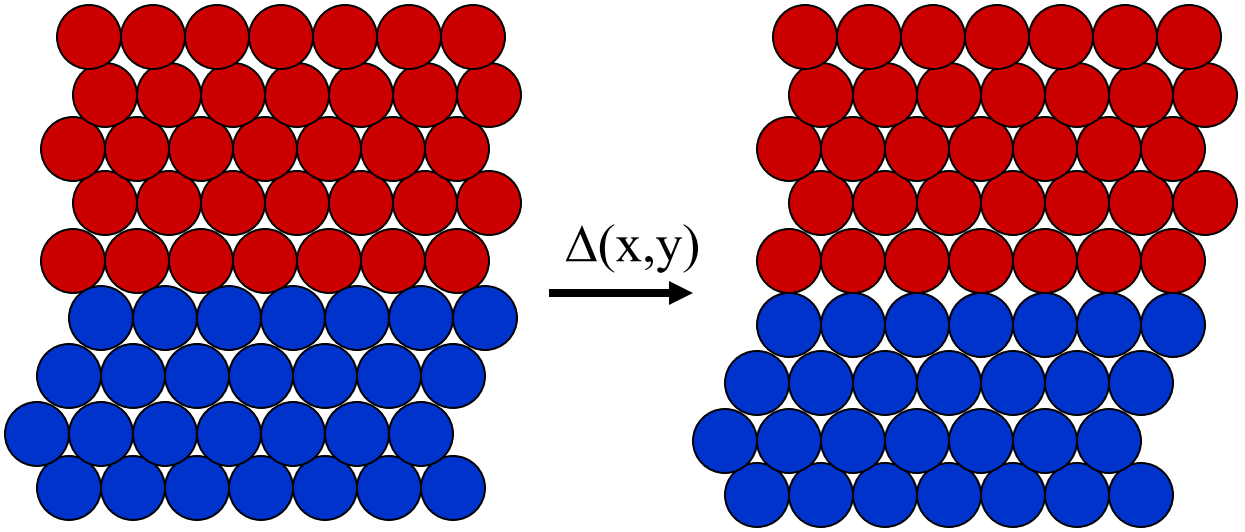


Region of the stacking fault



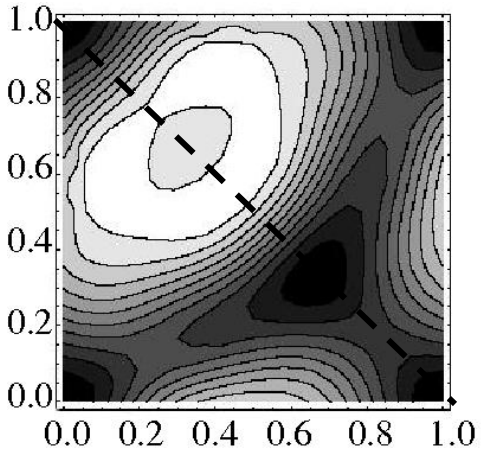
b_2 and b_3: partial dislocations
b_1: dislocation

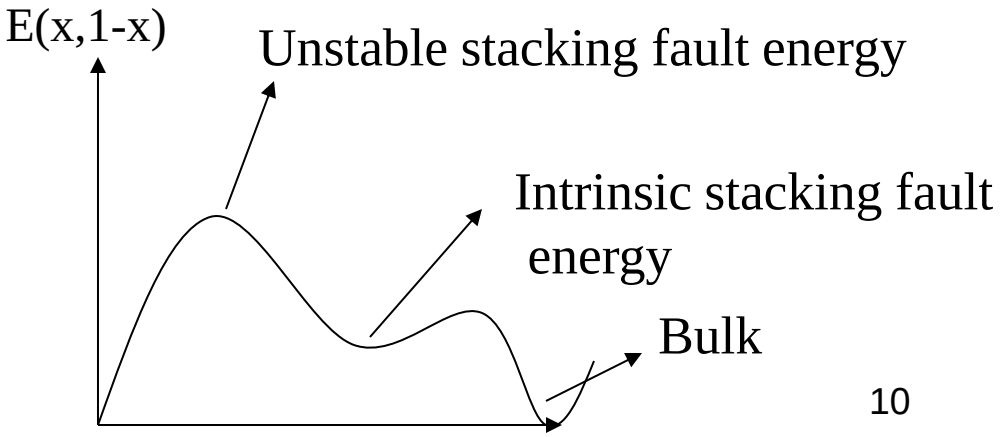
Generalized Stacking Fault Energy Surface
γ-surface: E(x,y)



1. Energy required to slip one half of a crystal with respect to the other by $x*a_1+y*a_2$
2. Exhibits periodicity of the unit cell (a_1,a_2) in the plane separating the two halves

Example:





Stacking fault expansion (T≠0): Statistical Thermodynamics

$$F = E + F_{config} + F_{vib}$$

Free energy of a crystal has 3 components:

(a) Internal energy: Total energy from DFT

(b) Configurational entropy: Obtain from the DFT γ-surface

Approximate energy basins in the γ-surface with

$$E(x,y) = E_o + K((x-x_o)^2 + (y-y_o)^2),$$

Free energy is then,

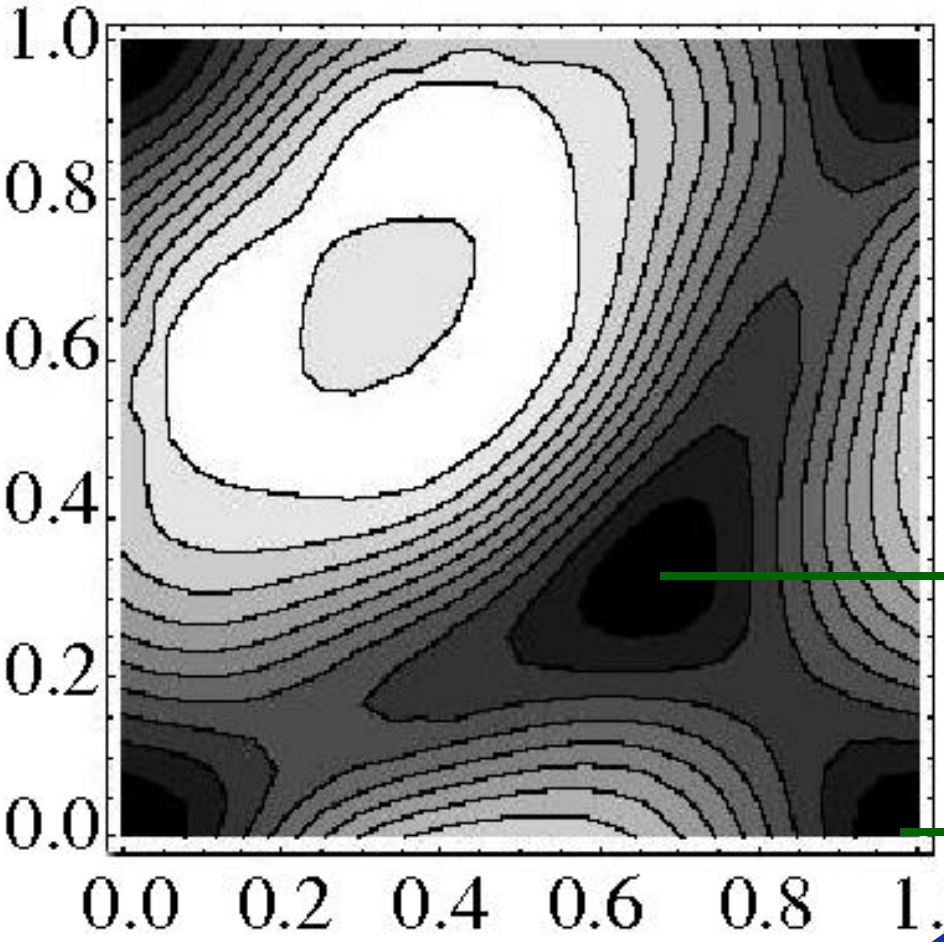
$$F_{conf} = -k_B T Log(\frac{K}{2\pi k_B T})$$

(c) Vibrational entropy: Obtain from phonons using DFT

$$F_{vib} = +k_B T \sum_{iq} Log(2sinh(\frac{\hbar\omega_{iq}}{2k_b T}))$$

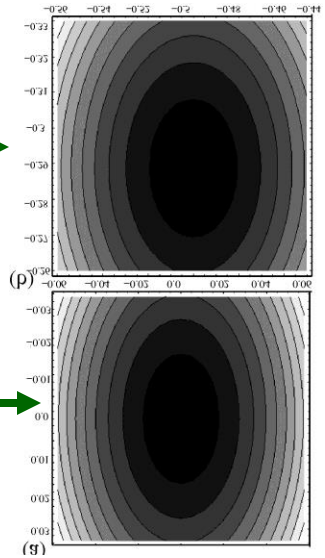
(a) Gives very low SFE (1 mJ/m^2) (earlier first-principles works).

The γ surface of 4H-SiC



Two energy basins :

(a) perfect (0,0) and
(b) faulted, (2/3,1/3)



(b)

(a)

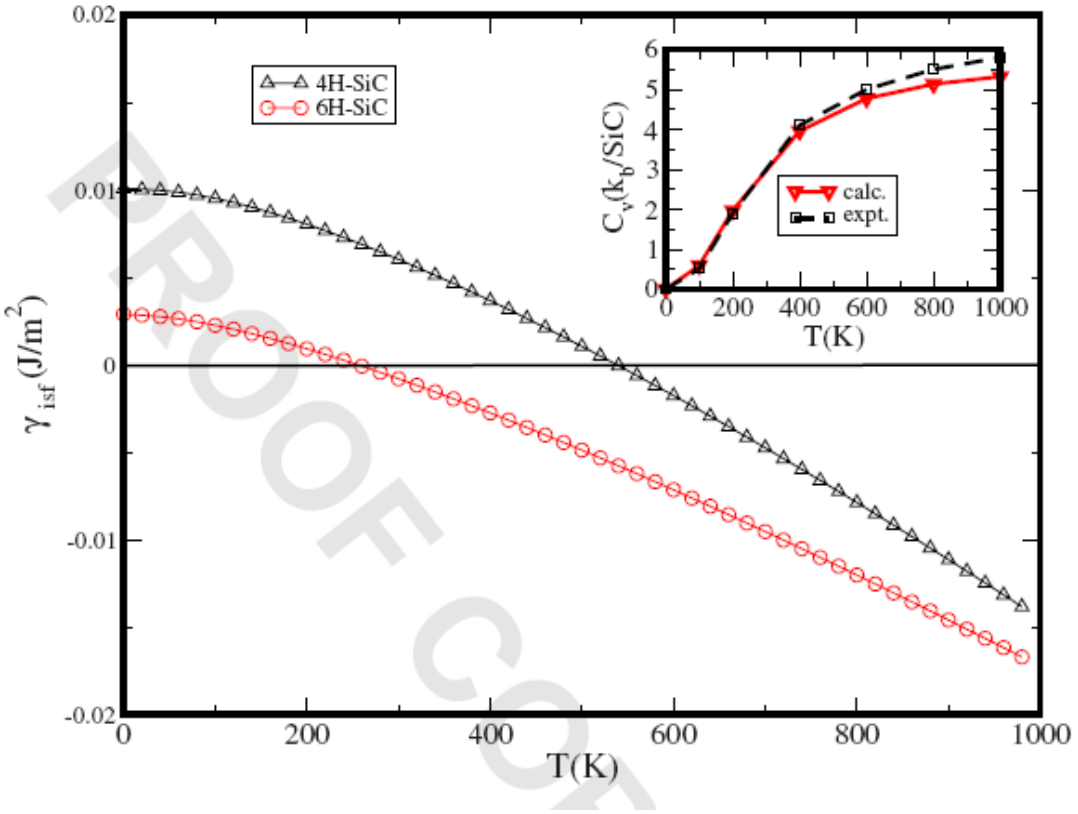
$$\gamma_s(T) = \gamma_s(0) + \Delta F_{conf}(T) + \Delta F_{vib}(T)$$

TABLE I. Calculated and experimental estimates of intrinsic (γ_{isf}) and unstable (γ_{us}) stacking fault energies for the slip in glide plane.

System	γ_{isf} (calculated) (mJ/m^2)	γ_{isf} (experimental) (mJ/m^2)	γ_{us} (J/m^2)
Si	46.9	69 (Refs. 26 and 27)	1.7
C	250	279 (Refs. 27 and 28)	5.5
Ge	48.5		1.6
3*C*-SiC	10.1		2.8
4*H*-SiC	9.1	14.7 ± 2.5 (Ref. 11)	2.9
6*H*-SiC	2.6	2.5 ± 0.9 (Ref. 12)	2.9

Ref. Thomas, Pandey and Waghmare, Phys Rev B (Rapid Comm), 77, 121203 (08)

Stacking fault energy of 4H-SiC



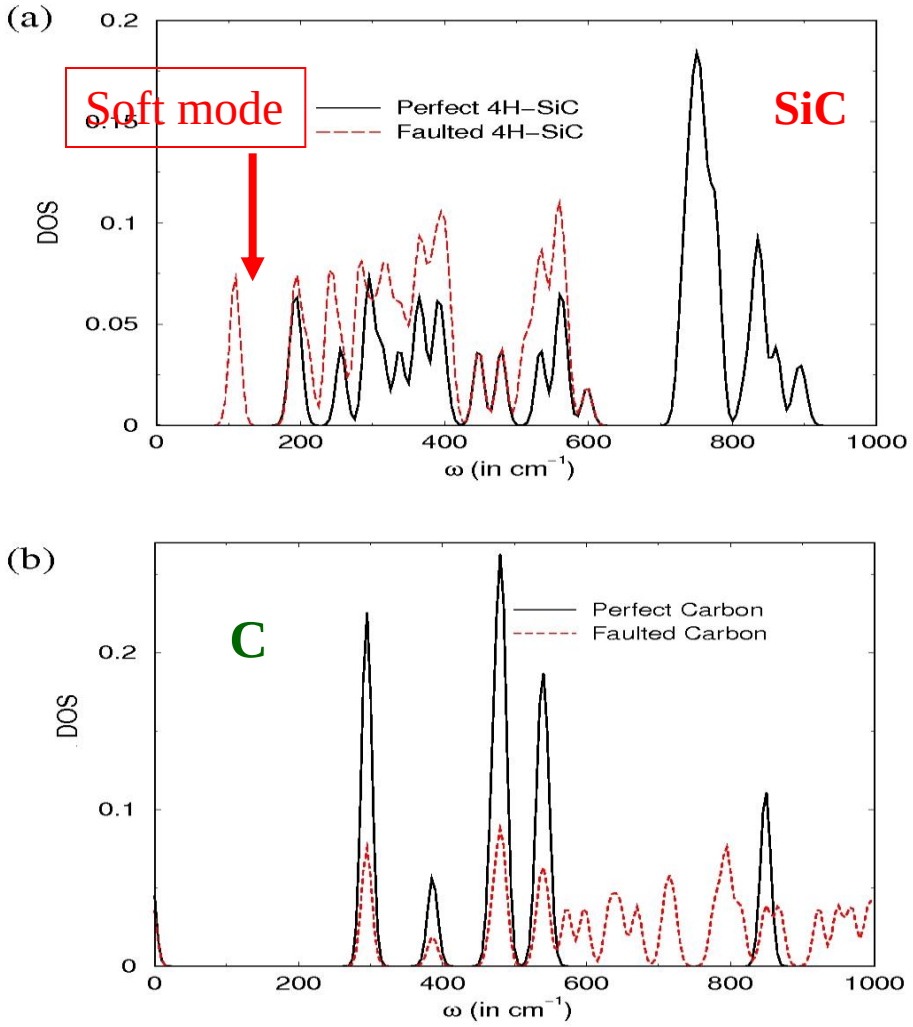
(1) Vibrational contribution to ΔF/T of (0.2×10-3 J/m^{2}K) dominates over the configurational contribution of (0.27×10-5 J/m^{2}K).

(2) γs(T) <0 for T > 60 K

► the faulted structure stabilized,
yielding the observed stacking fault expansion.

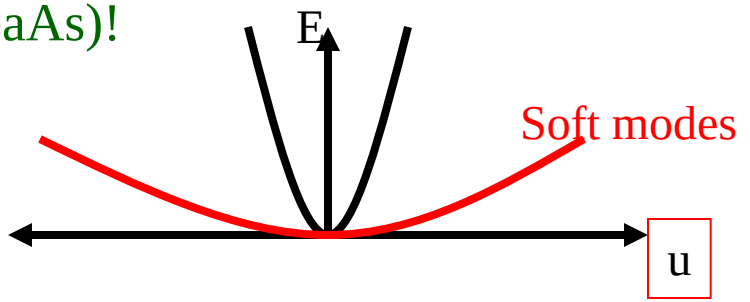
Origin of Observed Stacking Fault Expansion in 4H-SiC

Phonon DoS



Soft modes at 107.3, 107.4, 109.9 and 110.0 cm^{-1} in faulted 4H-structure of SiC

No such modes in Carbon (or Si, Ge, GaAs)!

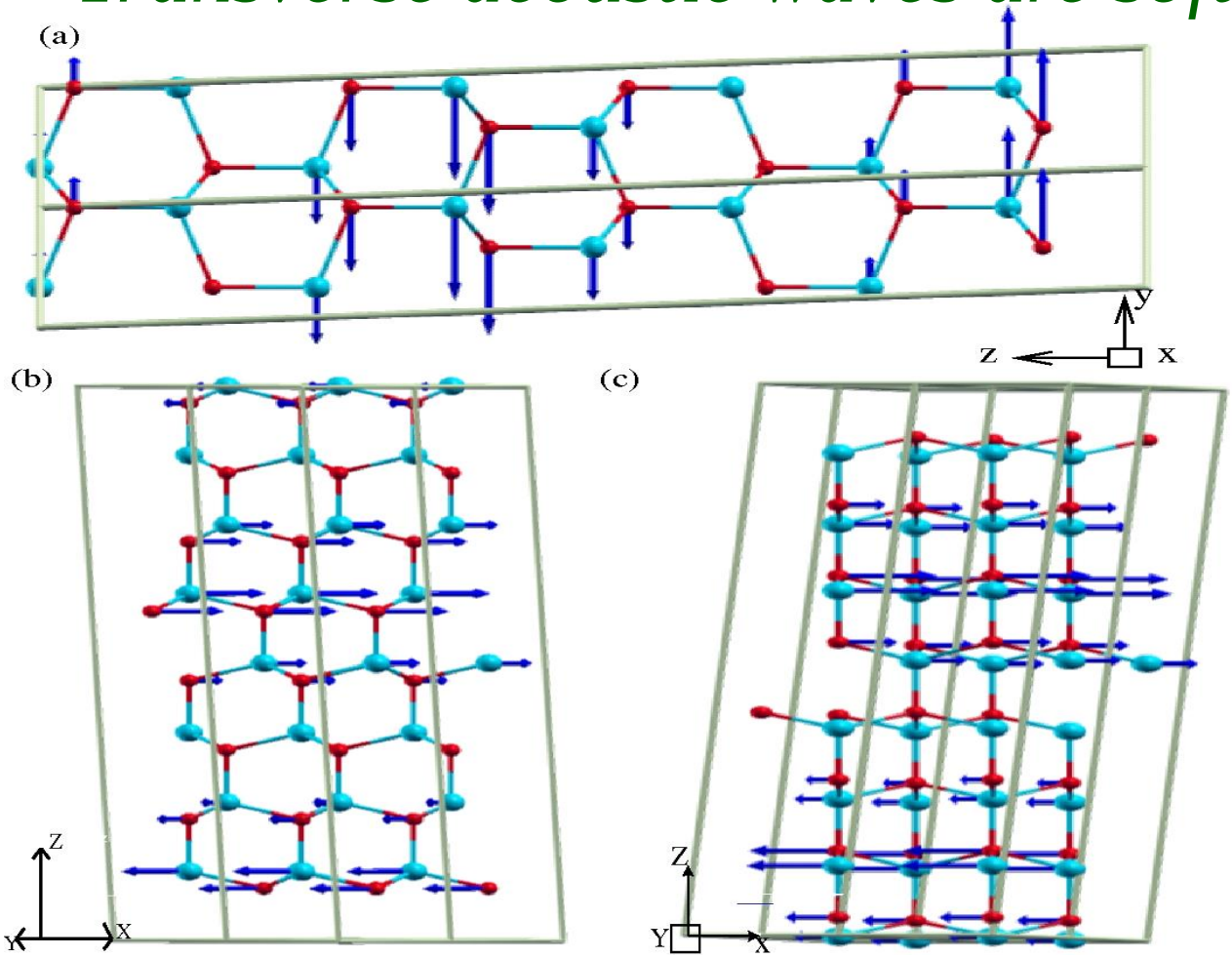


Soft modes: greater entropy

Soft phonon modes commonly responsible for structural phase transitions in solids. Here, we discover them in the context of stacking fault expansion.

Soft modes: Shear straining

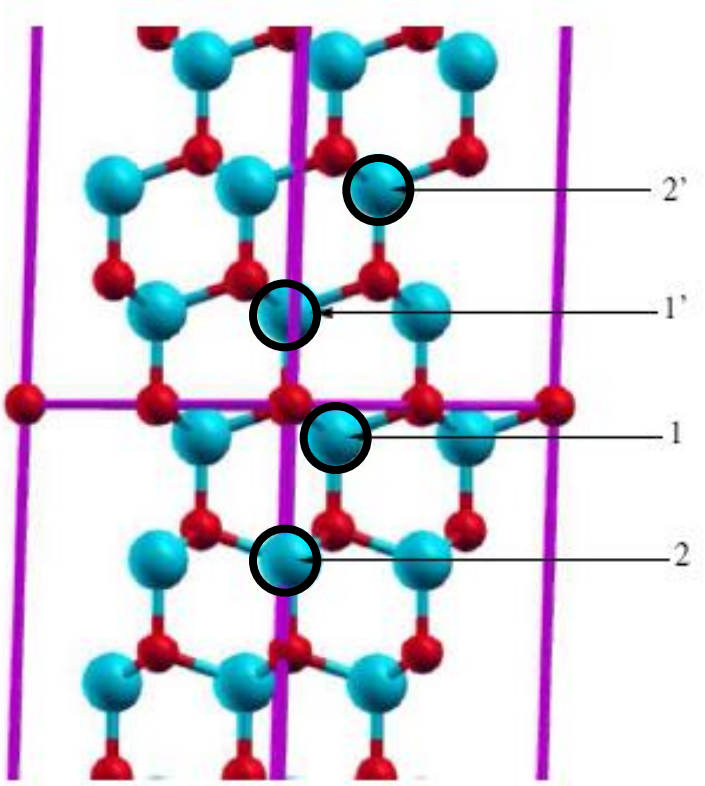
Transverse acoustic waves are softened



Prediction to be verified experimentally: *Shear waves will be slown down.*

Can we stop the stacking fault expansion in SiC?

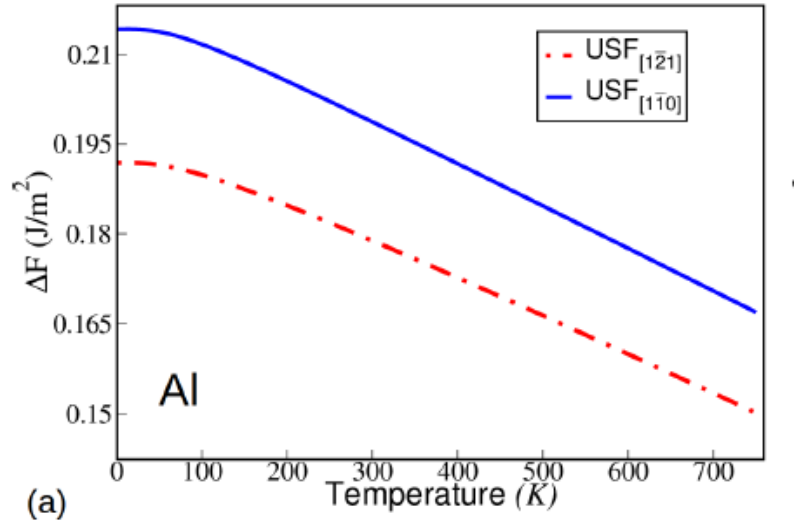
► *Through suitable substitutional doping to arrest it!*



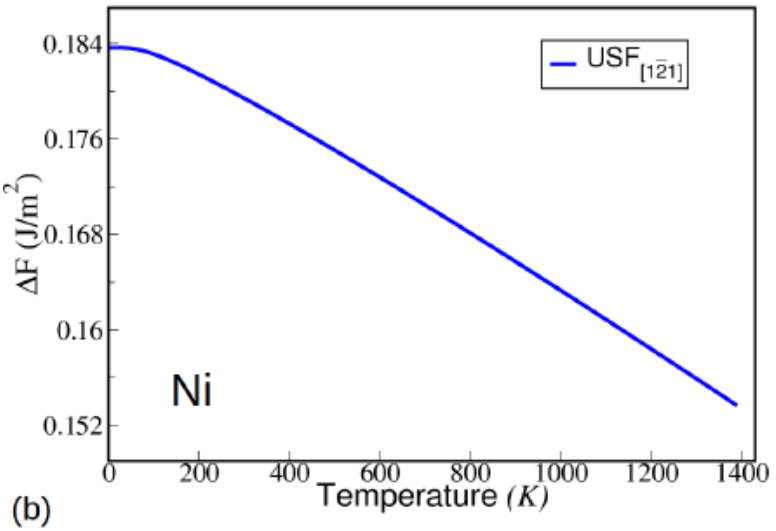
V and Cr doping in SiC results in higher SF energies, while also giving a DMS!

	TM	N	Fault (y/n)	Energy (meV) FM	Energy (meV) AFM	J (meV)	γ_{sf} (mJ/m^2) FM	γ_{sf} (mJ/m^2) AFM
6H	Cr	1	y	34.0	194.7	-160.7	16.6	35.5
			n	0.0	121.8	-121.8		
	Cr	2	y	253.2	261.1	-7.9	2.3	6.2
			n	245.2	248.3	-3.1		
	Cr	3	y	279.2	279.3	-0.1	24.9	24.6
			n	228.0	228.7	-0.7		
	Mn	1	y	0.0	57.1	-57.1	-62.1	-8.4
			n	127.4	74.3	53.1		
	Mn	2	y	335.0	335.0	0.0	18.8	17.2
			n	296.5	299.6	-3.1		
	Mn	3	y	358.1	357.6	0.5	29.2	28.0
			n	298.1	300.1	-2.0		
	V	1	y	38.0	—	—	18.5	—
			n	0.0	—	—		
	V	2	y	372.5	377.7	-5.2	15.8	12.3
			n	340.0	352.5	-12.5		
	V	3	y	387.5	399.7	-12.2	20.2	22.2
			n	346.1	354.0	-7.9		

Unstable Stacking Fault Energies in Metals



(a)



(b)

Energy release rate
for nucleation of dislocations

20-25 % reduction as
T increases to 0.8 T_m

In Cu, the configuration is
unstable!

Enhanced ductility

Bhogra, Ramamurty and Waghmare, JPCM (2014)

Why Phonons?

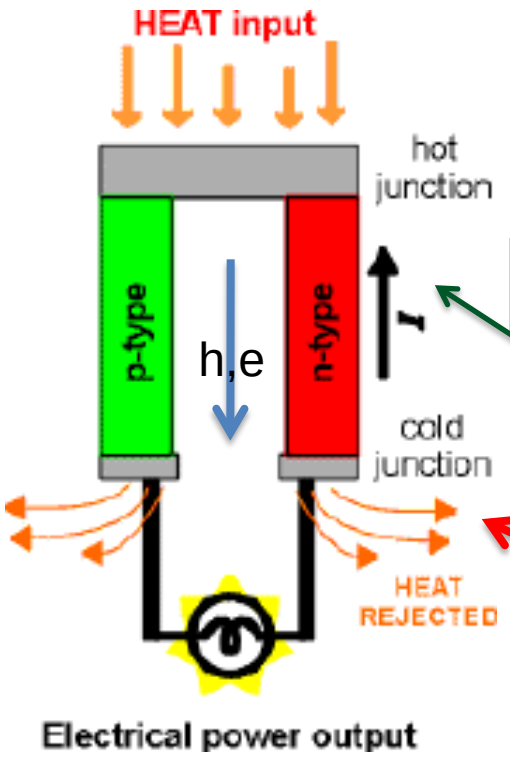
- Fingerprint of a material: Raman, IR spectra
- Thermodynamic stability: vibrational entropy T, soft modes
- *Properties: elastic, dielectric, piezoelectric, etc (couple with fields)*
- Structural Transitions: instabilities of a structure $w \rightarrow 0$
- Phonons coupled with electrons, spin, exciton, polarons; e.g. superconductivity

Thermoelectrics and energy conversion

Directly convert thermal energy to electrical energy

Environmentally friendly, No moving parts (except for a fan)

Seebeck Effect:



$\Delta V = S\,\Delta T$

Figure of Merit:

$$ZT = \frac{S^2 \sigma}{k_e + k_p} T$$

It should carry electric current, but NOT heat (dominated by phonons)

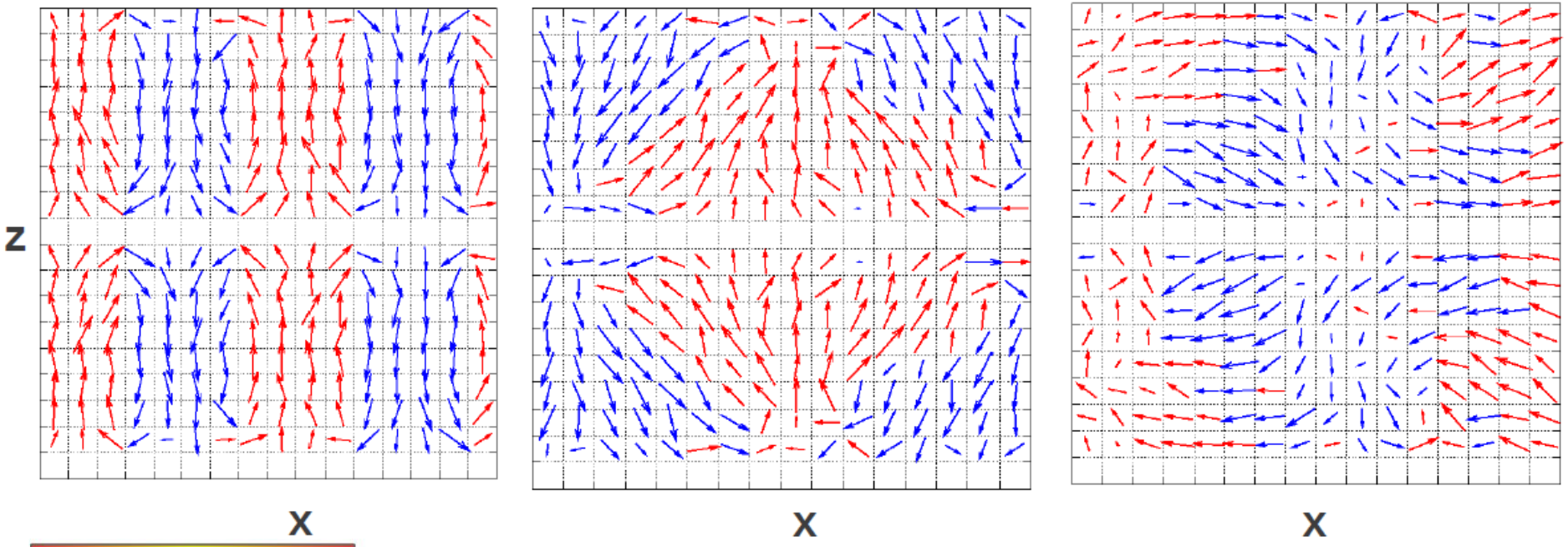
A key to designing high ZT materials is to *manipulate* transport of phonons and electrons*: low k*

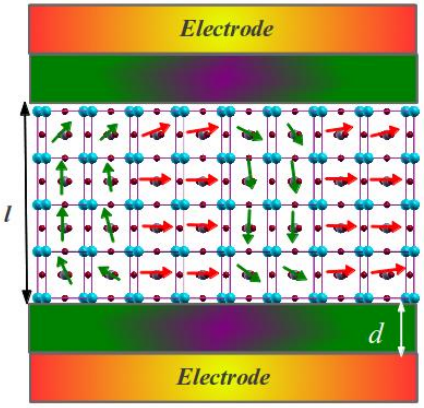
Properties of Ferroelectric Domains

Strain Engineering of Domain Structure in epitaxial $PbTiO_3$

Compressive → Tensile

η = -0.02 | η = -0.005 | η = 0.01

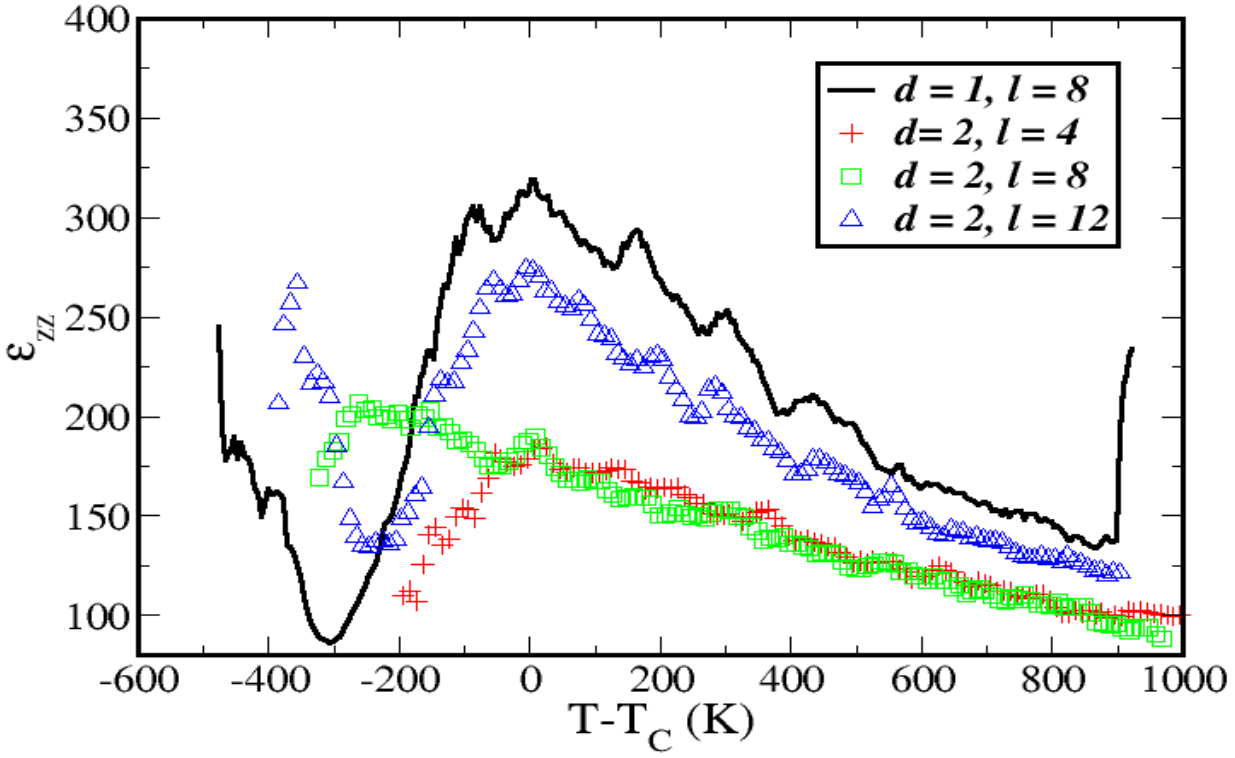




Imperfect electrodes influence ordering of polar phonons

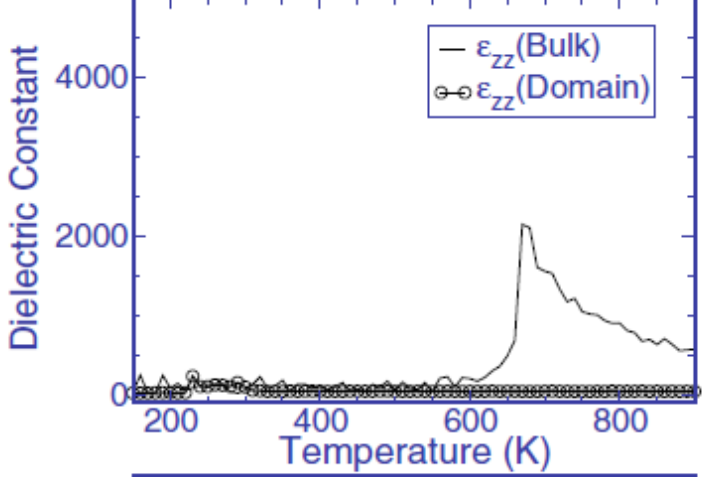
Kouser, Nishimatsu, Waghmare,
Phys. Rev. B **88**, 064102 (2013); PRB Kaleidoscope, Aug (2013)

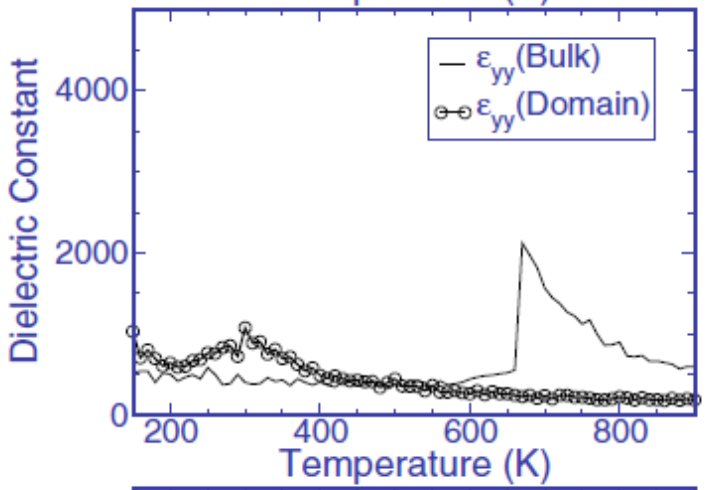
Diffuse Dielectric Response of Domain Structure ($PbTiO_3$)

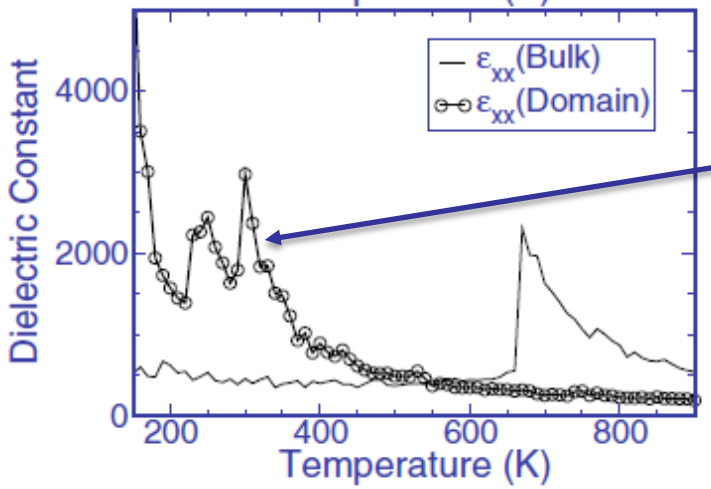


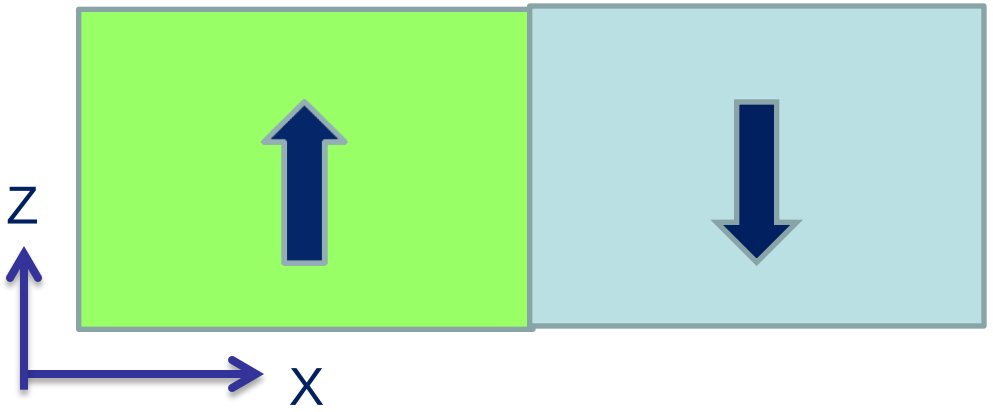
Ordering to inhomogeneous phase leads to a diffuse dielectric response across the transition

Dielectric Response of a 180° Ferroelectric Domain in $PbTiO_3$





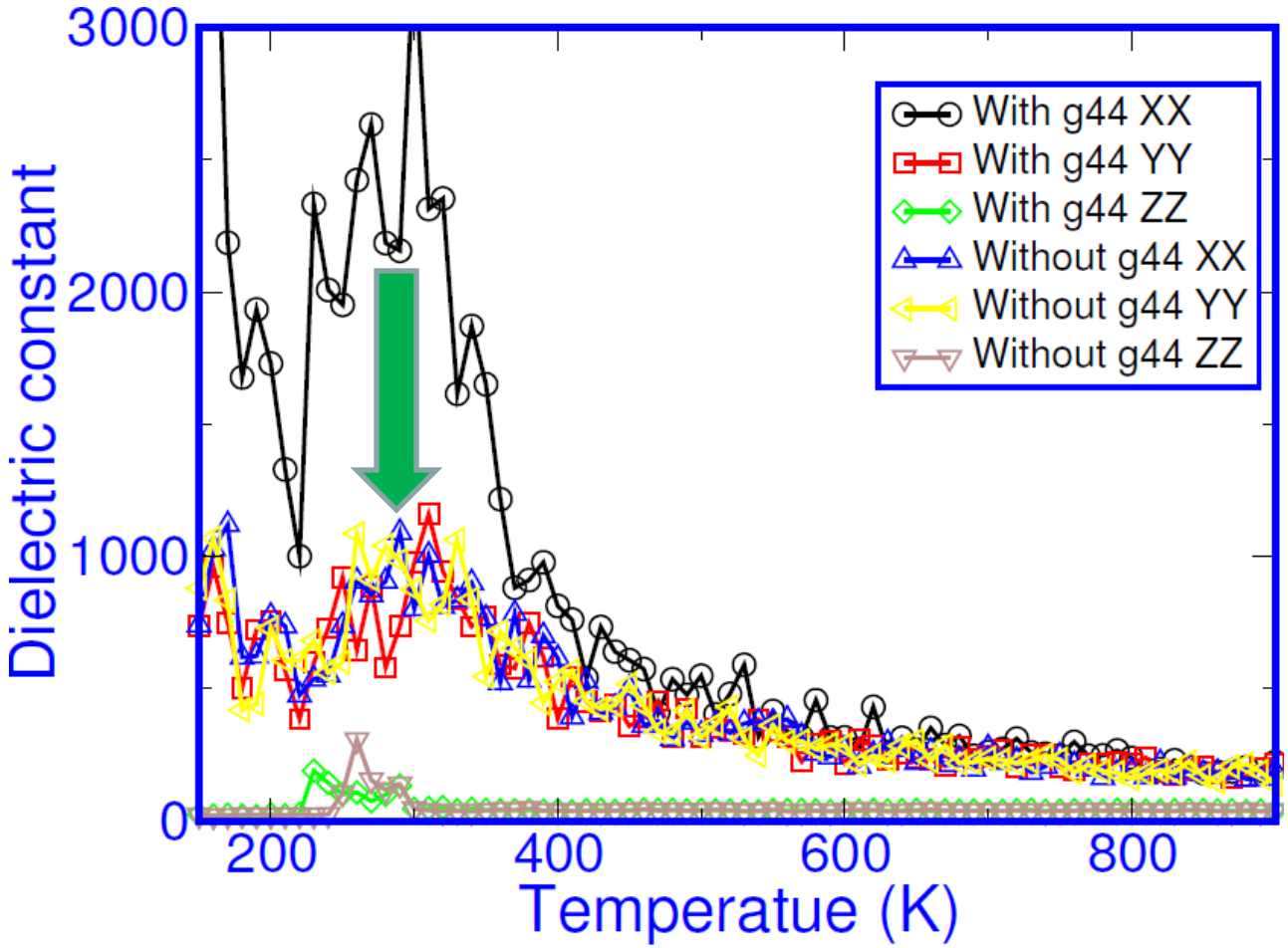




Enhanced Dielectric Response
In the direction perpendicular to the domain wall!

Why xx component?

Corroboration of the phen. Theory from MD



Strain-phonon coupling: dielectric response of a domain wall

Thank you!