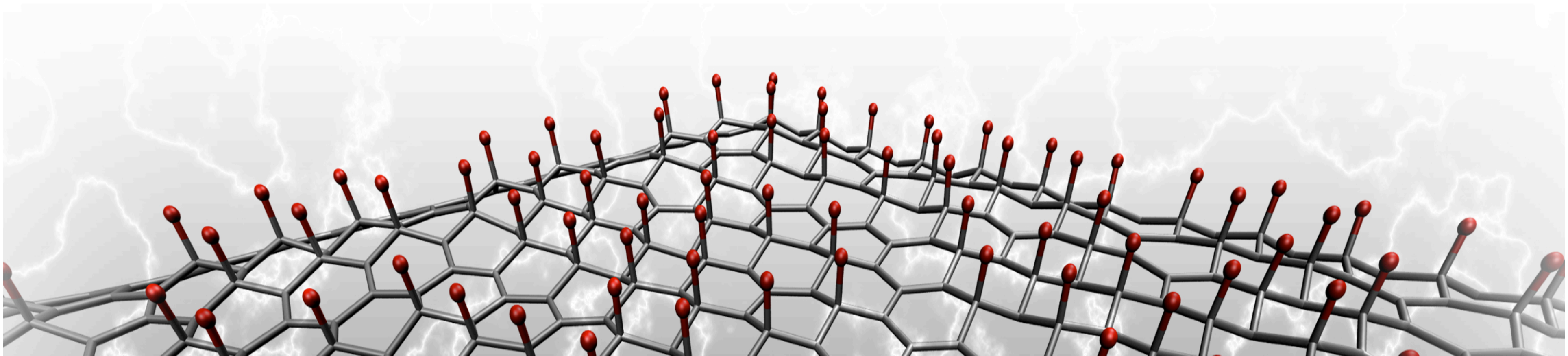

Phase Change and Piezoelectric Properties of Two-Dimensional Materials

April 16, 2015

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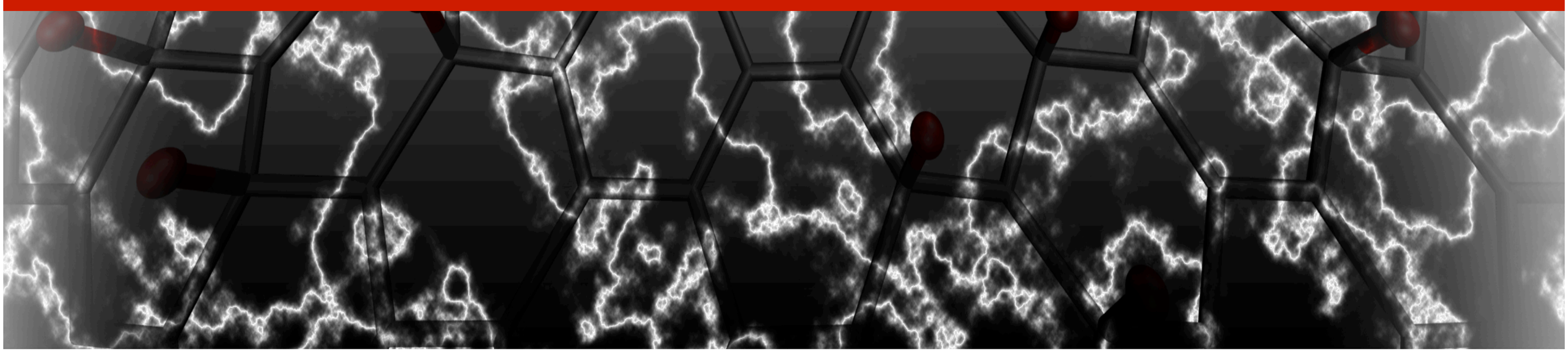
Department of Materials Science and Engineering
Stanford University



CONCLUSIONS

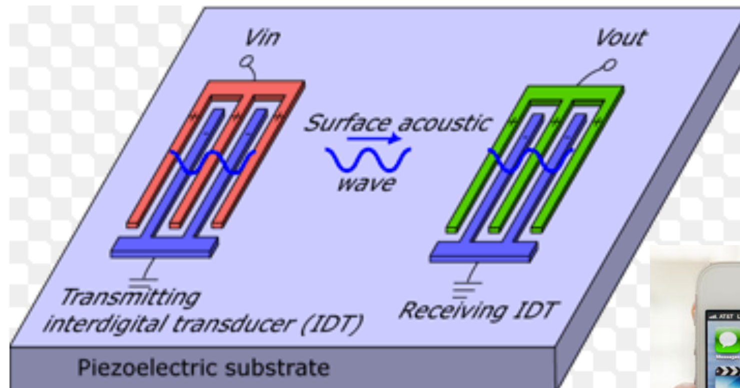
- Many monolayer materials exhibit emergent piezoelectricity, e.g. MoS_2
  - Duerloo, Ong, Reed, *J. Phys. Chem. Lett.* **3**, 2871 (2012).

- We discover that some single-layer materials (e.g. $MoTe_2$) exhibit structural metal-insulator phase transitions under tensile strains and high temperatures from 930K to room T.
  - Duerloo, Li, Reed, *Nat. Comm.* **5**, 4214 (2014);
  - Duerloo, Reed, in review (2015).

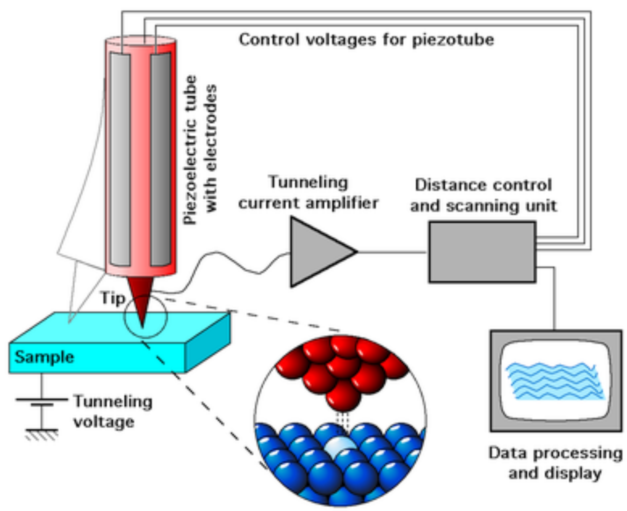
PIEZOELECTRIC MATERIAL APPLICATIONS

Stress Sensors

Acoustic transducers for signal processing

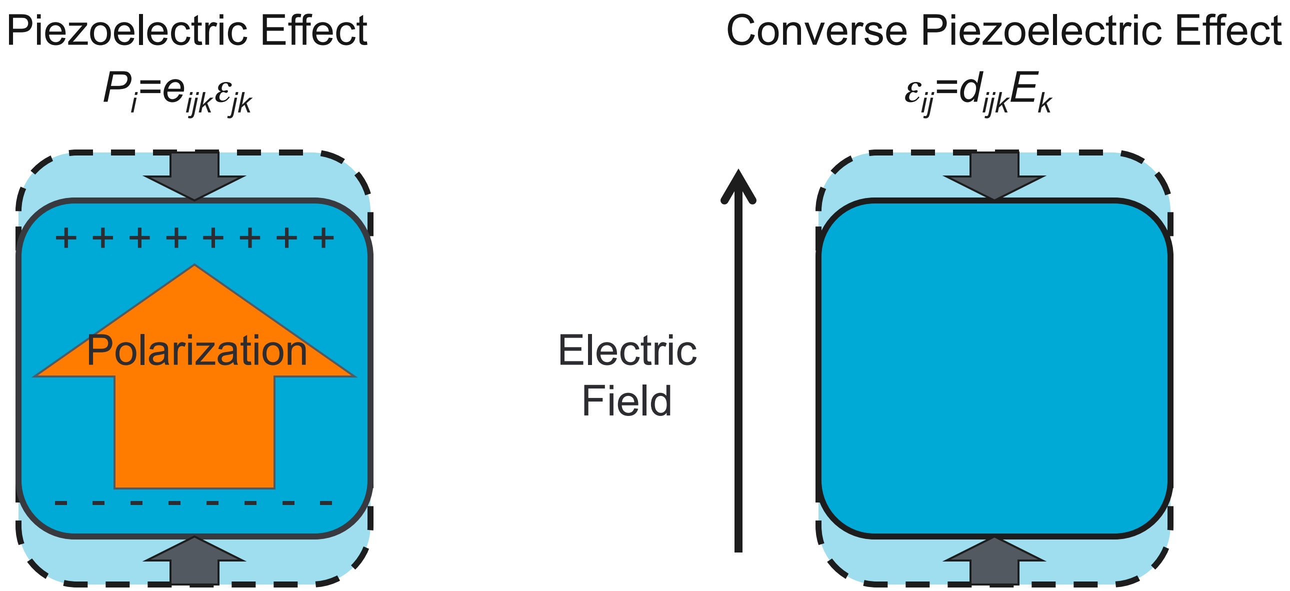


Scanning Tunneling Microscope (STM)



Injet Printing

PIEZOELECTRICITY



Piezoelectric materials must exhibit:

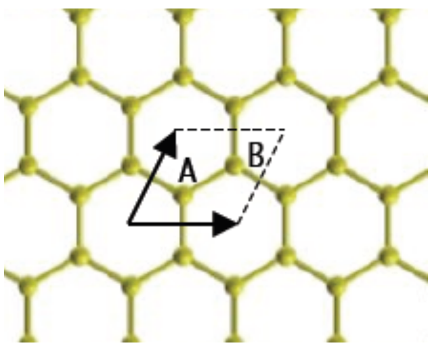
1. An electronic bandgap
2. A lack of centrosymmetry

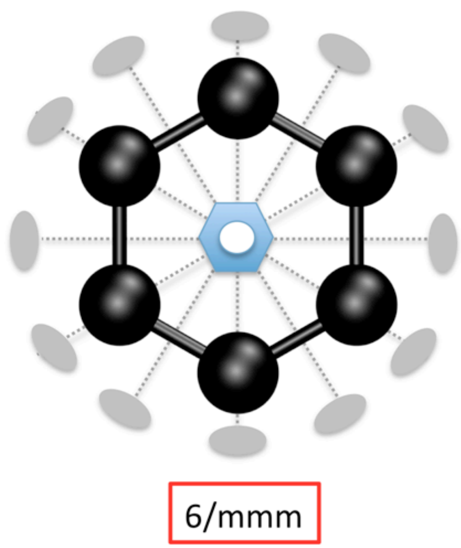
Inversion symmetry of a crystal => $d_{ijk} = (-1)^3 d_{ijk} = -d_{ijk}$

So $d_{ijk}=0$ for crystals with inversion symmetry!

GRAPHENE IS NOT PIEZOELECTRIC

graphene





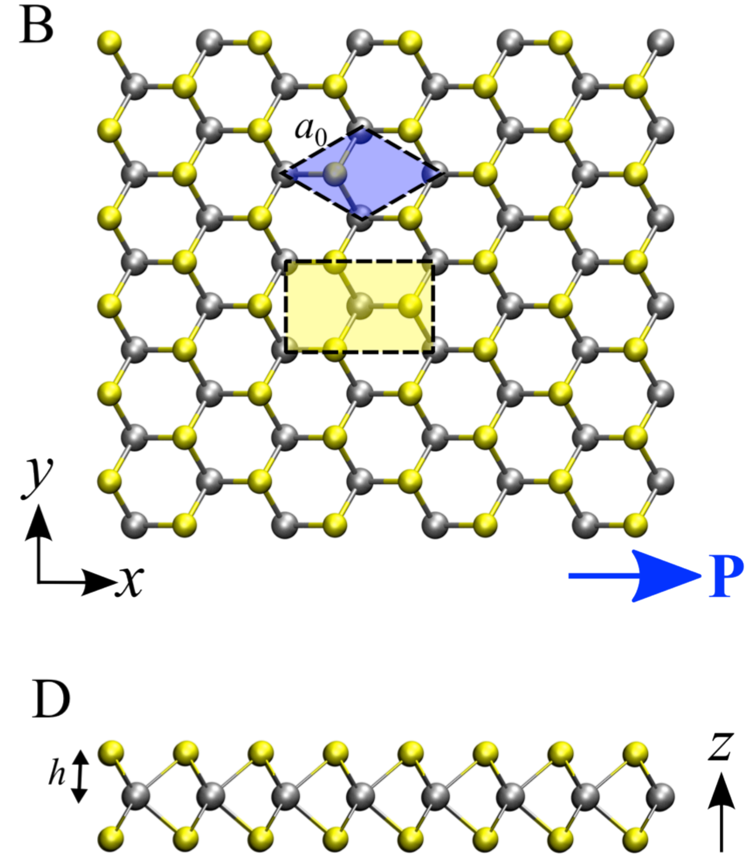
- ***Inversion symmetry => non-piezoelectric***
- ***Semi-metallic character => non-piezoelectric***

TMD MONOLAYERS HAVE POTENTIAL FOR PIEZOELECTRICITY

Transition Metal Dichalcogenides:

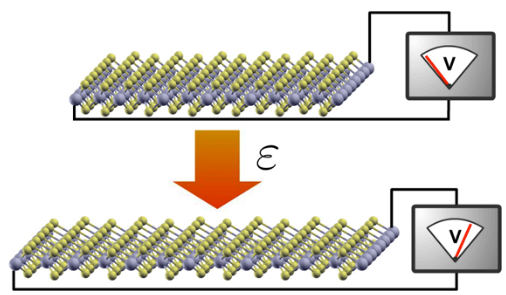
MoS_2, $MoSe_2$. $MoTe_2$, WS_2, WSe_2

Trigonal prismatic structure:

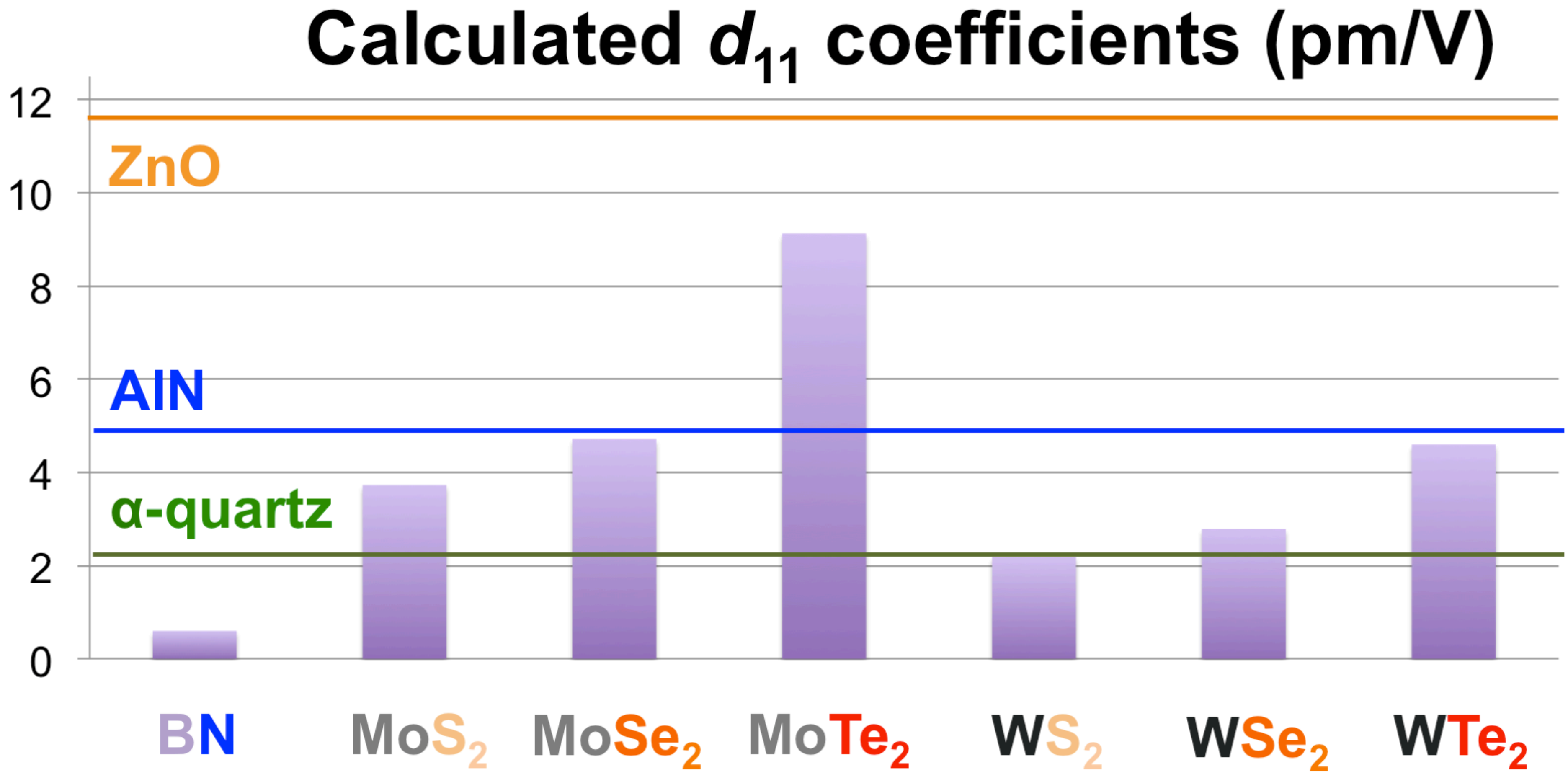


- ✓ Semiconducting (E_{gap} ~ 1-2 eV)
- ✓ Not centrosymmetric
  - ✓ 3m point group leads to non-zero d_{11} and e_{11} coefficients

$$\begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{xy} \end{bmatrix} = \begin{bmatrix} d_{11} & 0 & 0 \\ -d_{11} & 0 & 0 \\ 0 & -d_{11} & 0 \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$



WE DISCOVER THAT A VARIETY OF TMDS HAVE SIGNIFICANT PIEZOELECTRIC EFFECTS



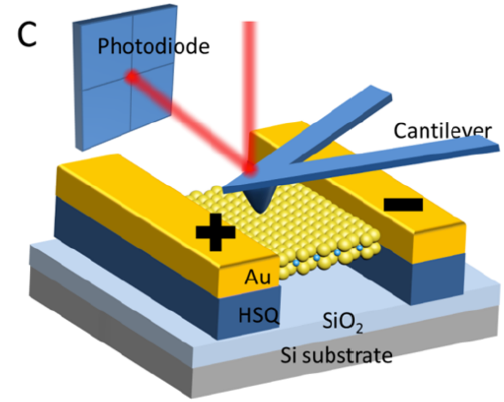
Piezo-coefficients of trigonal prismatic TMD structures are comparable to bulk wurtzite structures

K.-A. Duerloo, M. T. Ong, E. J. Reed., J. Phys. Chem. Lett. 3, 2871 (2012).

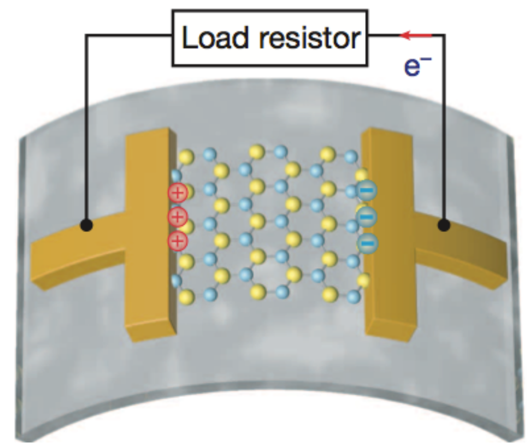
PIEZOELECTRICITY IN 2D MATERIALS HAS RECENTLY BEEN OBSERVED

"Observation of Piezoelectricity in monolayer MoS_2," Zhu, Wang, Xiao, Liu, Xiong, Wong, Ye, Yin, Zhang, *Nature Nanotechnology (2014).*

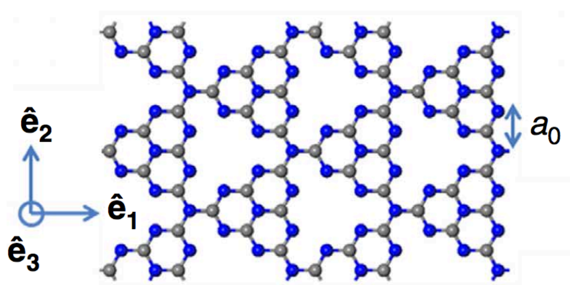
Reported e_{11} within 20% of predicted.



"Piezoelectricity of single atomic layer MoS_2…" Wu, Wang, Hone, Wang *et al.*, *Nature* (2014).

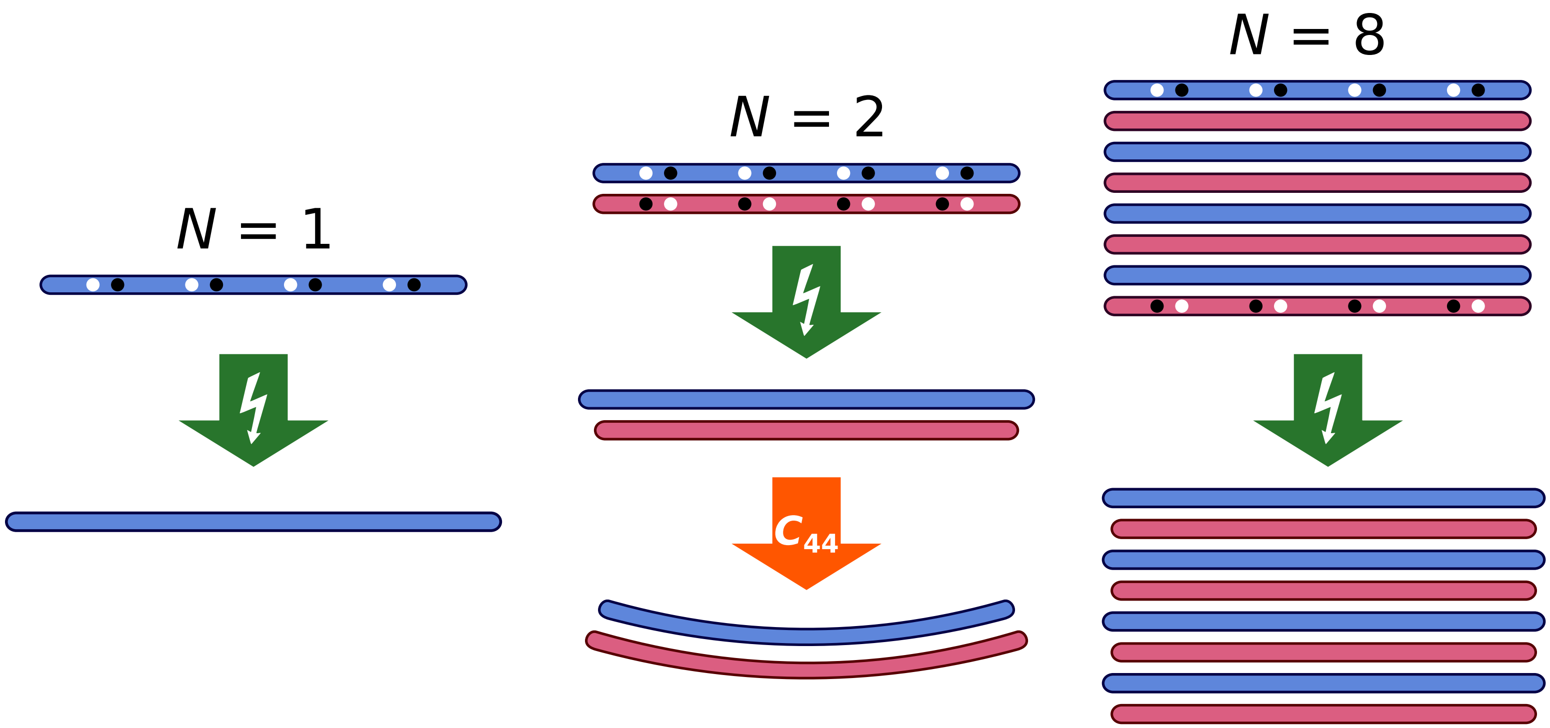


Piezoelectricity in C_3N_4 few layers: Zelisko, *et al*, Nature Communications (2014).



BILAYER EMERGENT ELECTROMECHANICAL CURVATURE

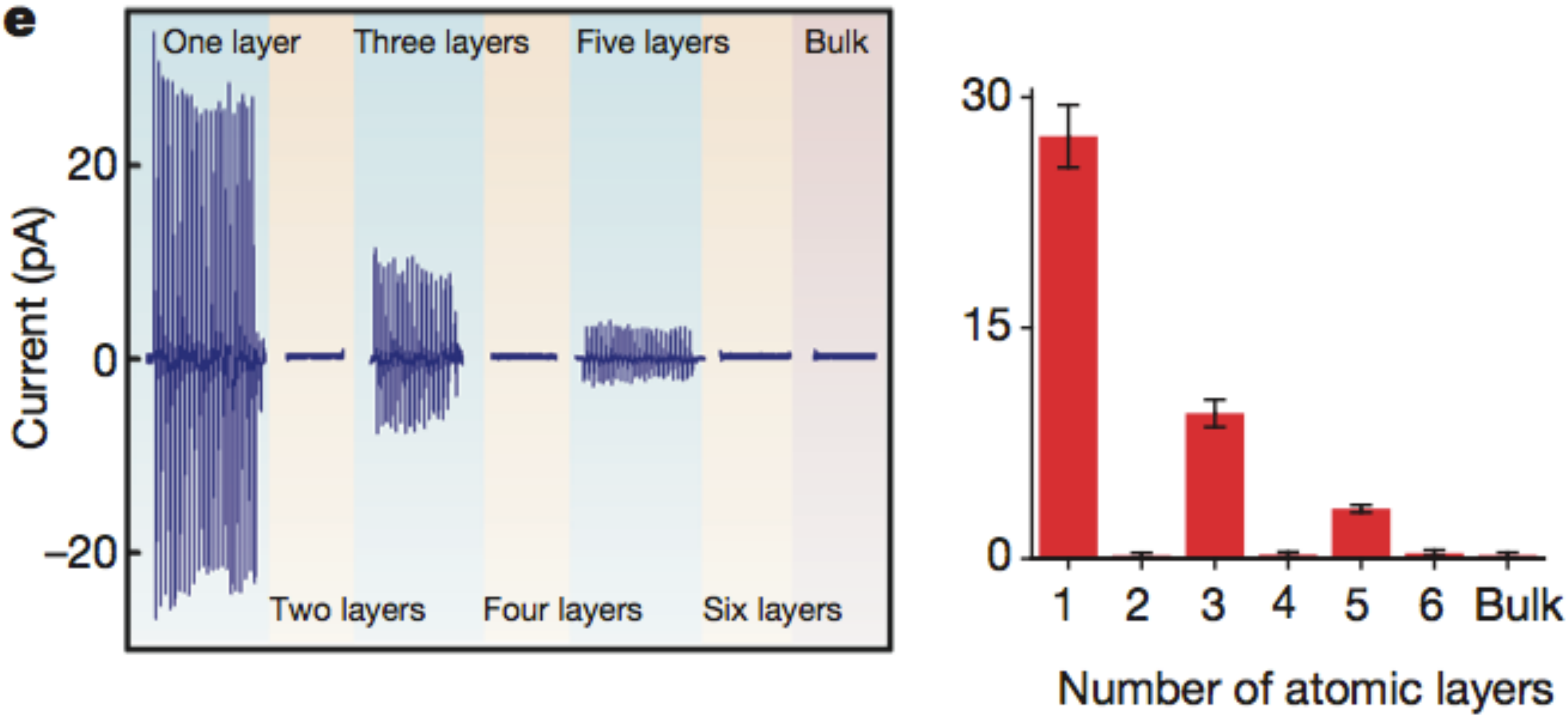
We find that TMDC monolayers are piezoelectric while their bulk host crystals exhibit an inversion center and are therefore not piezoelectric!



We predict bilayer BN exhibits an electromechanical curvature effect.

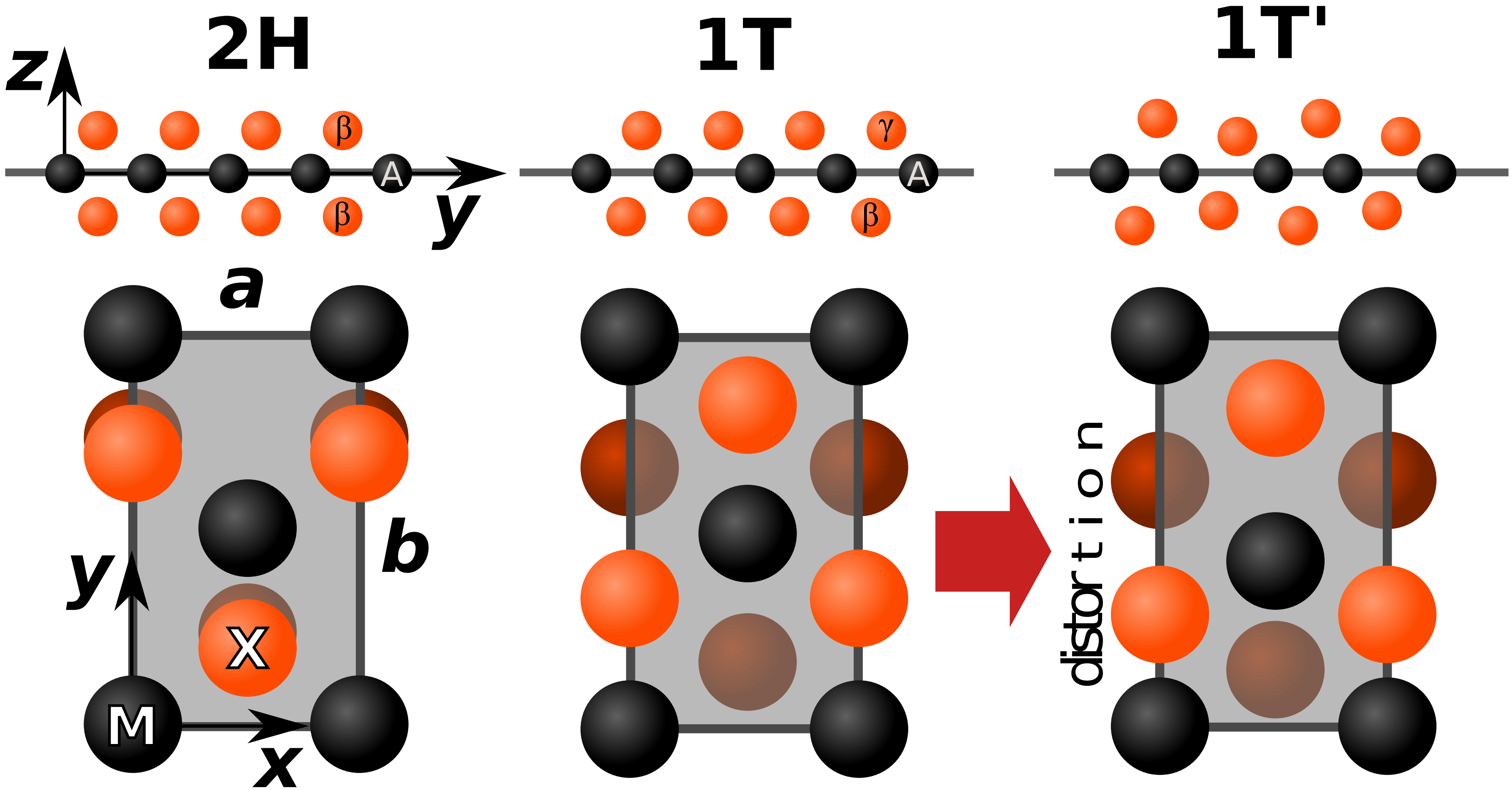
K.-A. Duerloo, E. J. Reed., Nano Letters (2013).

PIEZOELECTRIC EFFECTS OBSERVED ONLY FOR ODD NUMBERS OF LAYERS



Piezoelectricity of single atomic layer MoS_2..." Wu, Wang, Hone, Wang *et al.*, *Nature* (2014).

TMD MONOLAYERS CAN EXIST IN MULTIPLE CRYSTAL STRUCTURES

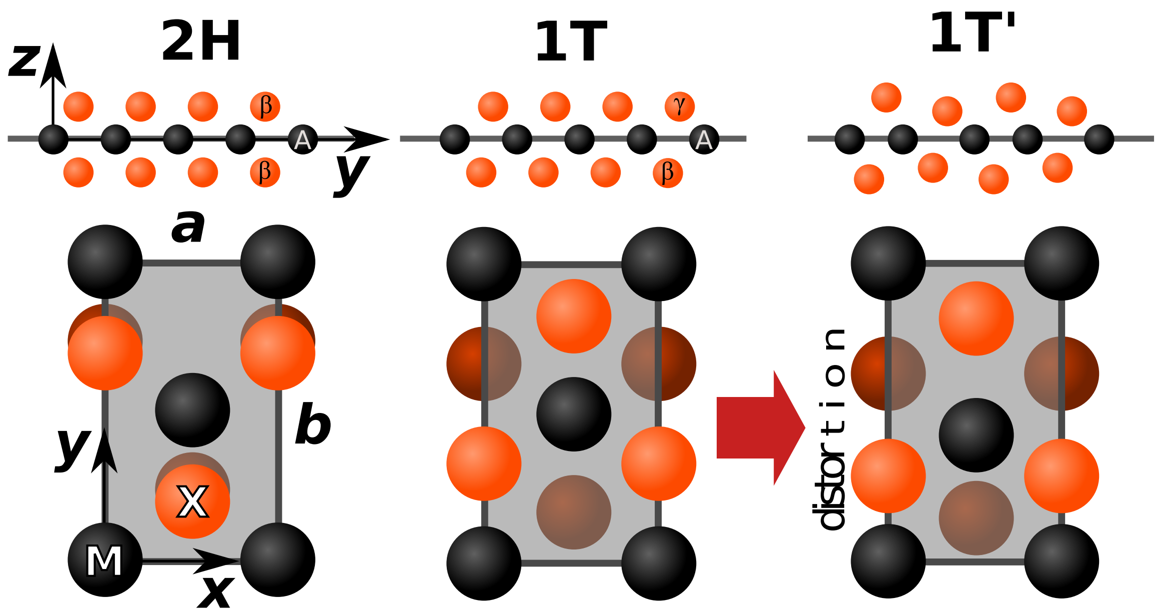


Semiconducting (1-2 eV)

Metallic

Semi-metallic

TMD MONOLAYERS MIGHT EXIST IN MULTIPLE CRYSTAL STRUCTURES

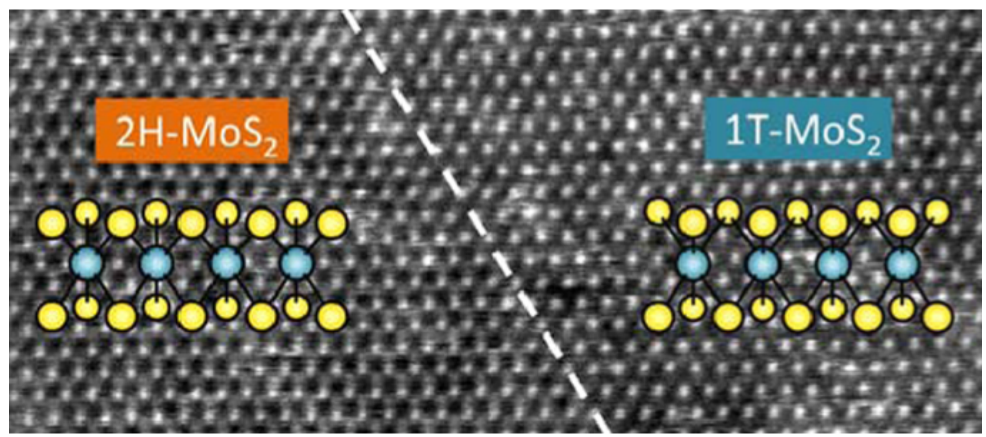


Semiconducting Metallic Metallic

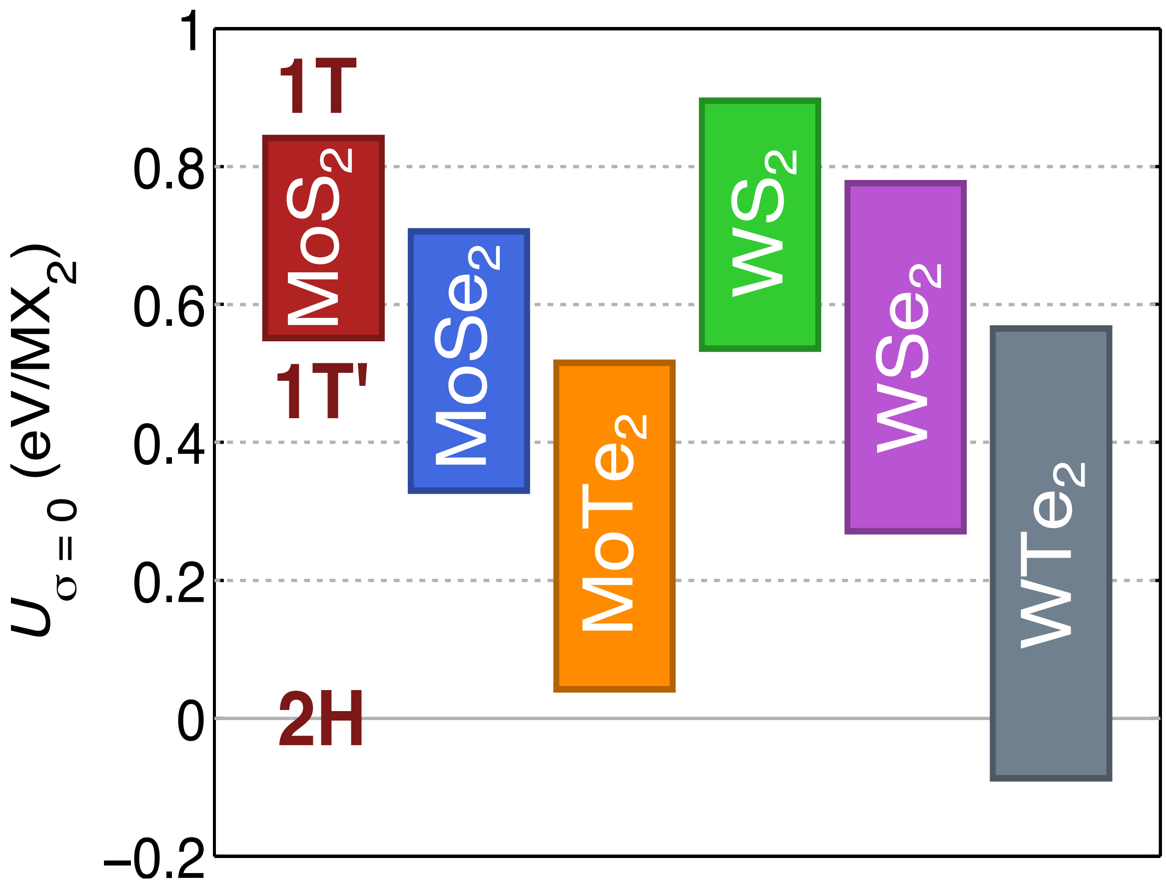
Can the phases of monolayers be engineered and employed in devices?

Two phases have been observed in chemically exfoliated MoS_2 and WS_2.

Eda et al, ACS Nano 6, 7311 (2012);
Voiry et al, Nat. Mat. (2013).

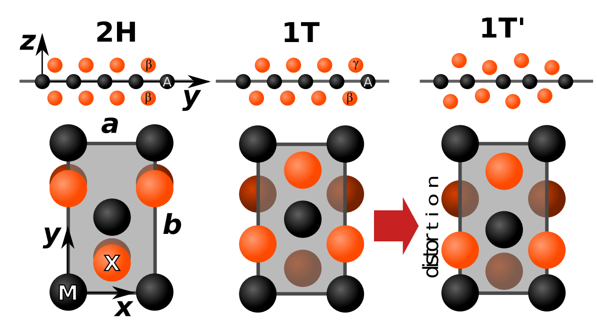


$MoTe_2$ AND WTe_2 EXHIBIT PHASE BOUNDARIES NEAREST AMBIENT

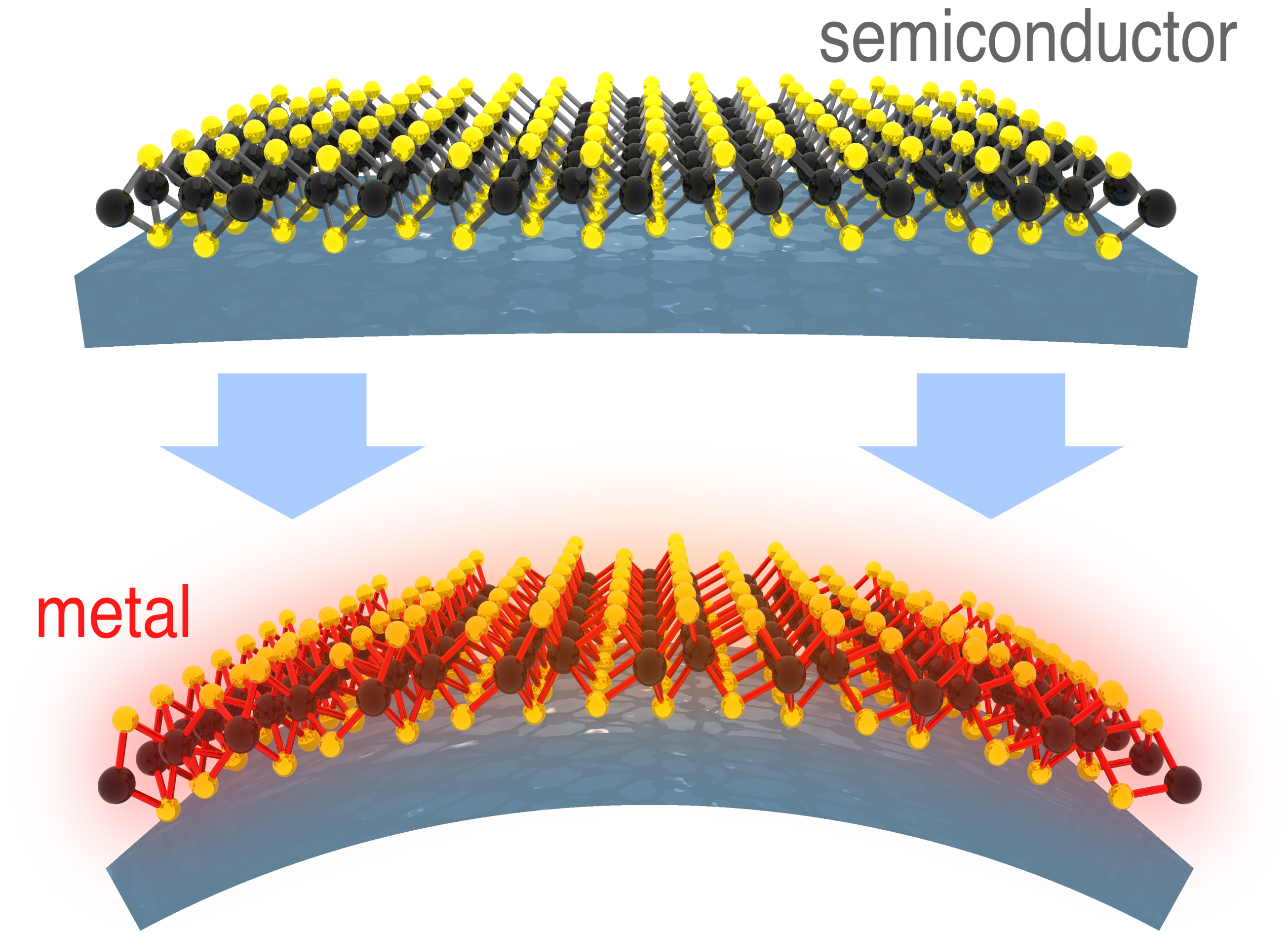


PBE EXC.
No phonons.

Our semi-local DFT calcualtions indicate $MoTe_2$ and WTe_2 exhibit the smallest 2H-1T' energy difference.

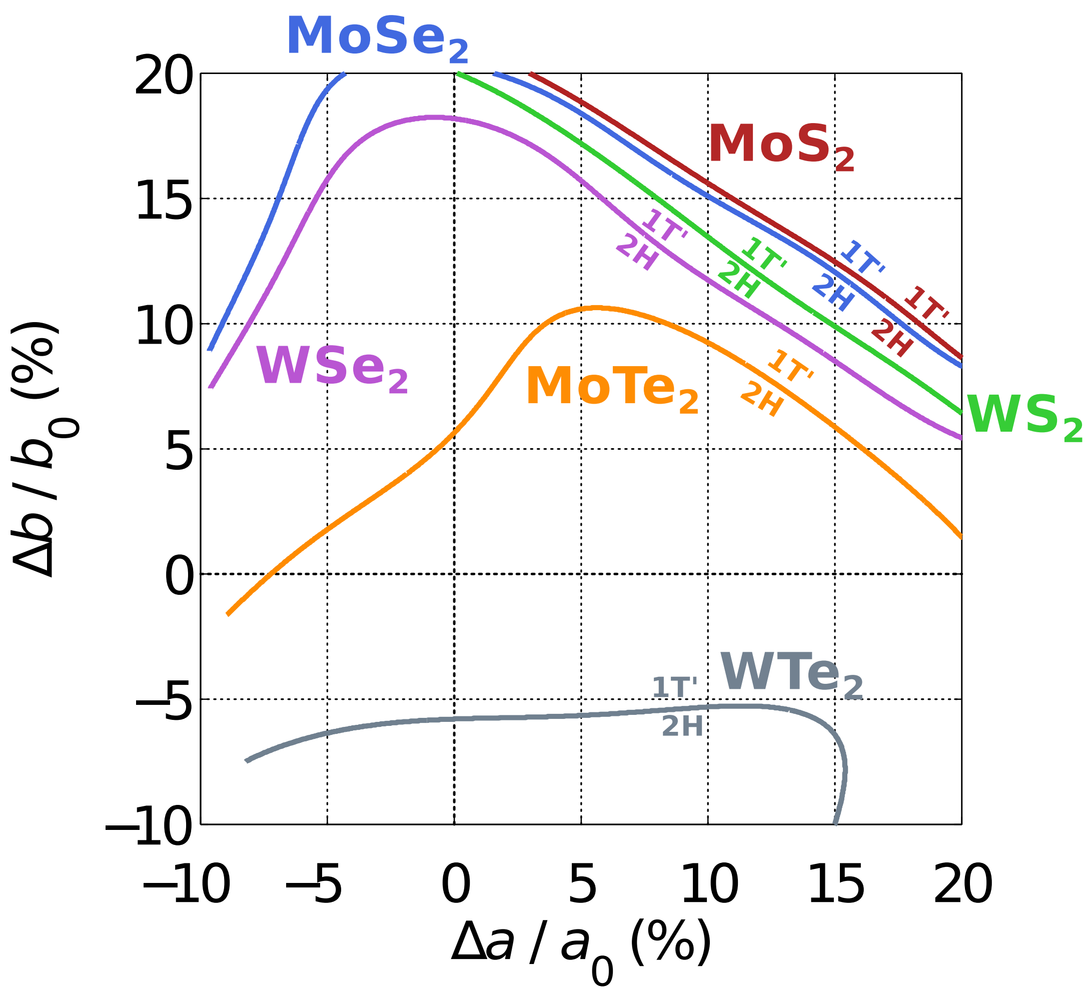


CAN TENSILE STRAIN CAUSE A STRUCTURAL PHASE TRANSITION?



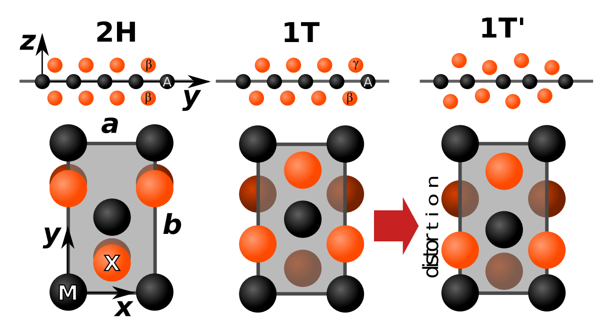
WE COMPUTE STRAIN PHASE BOUNDARIES FOR MONOLAYERS

Our DFT/PBE calculations of TMD monolayer phase boundaries in strain.



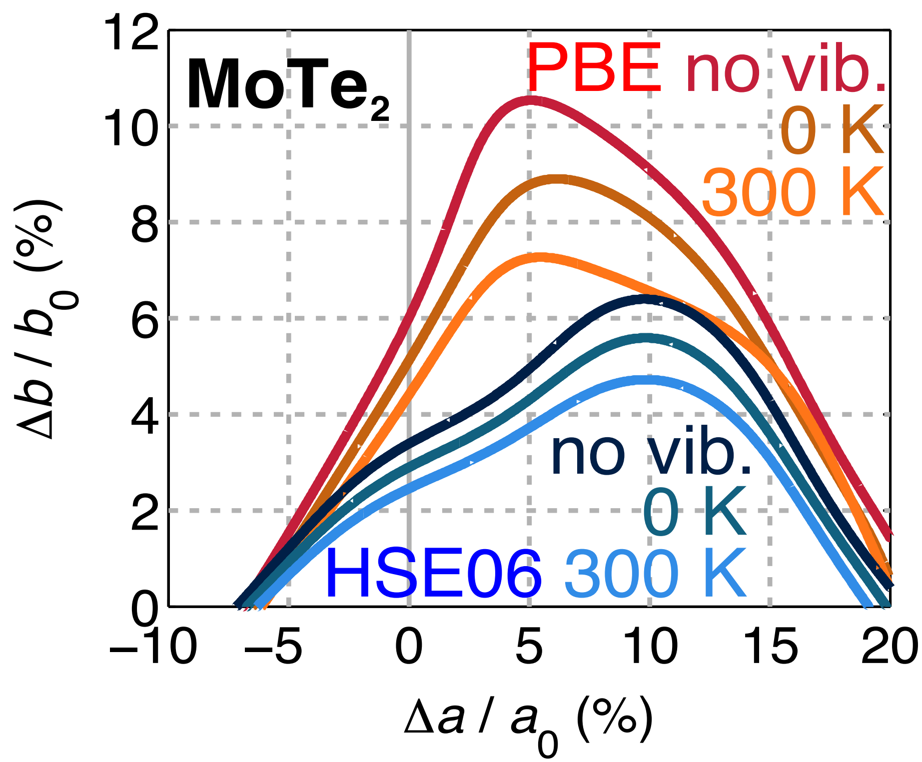
Energy calculations on a 5x5 grid in (a,b) lattice constants. Lagrange interpolation for phase boundaries.

Tensile strain of 6% along b axis croses phase boundary in $MoTe_2$.



Duerloo, Li, Reed, Nature Communications, (2014).

HYBRID EXCHANGE AND ENTROPIC EFFECTS IMPACT $MoTe_2$ BOUNDARY

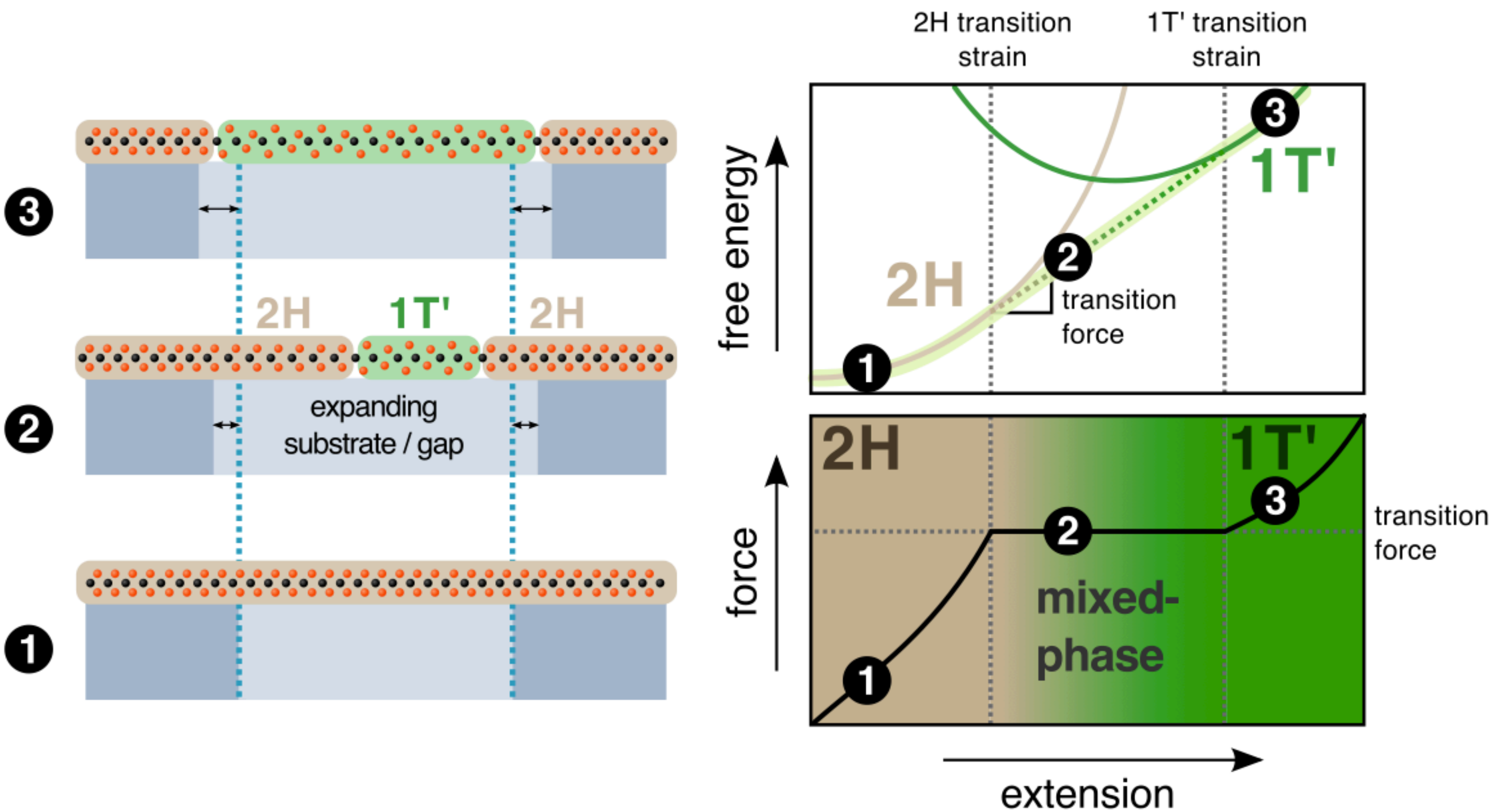


- Hybrid exchange (HSE06) moves phase boundary closer to ambient conditions
- Incorporation of entropic effects (F=E-TS) accomplished using quasiharmonic approximation with computed phonon bands

$$F(a,b) \approx U_{\mathrm{crystal}}(a,b) + \sum_i \left[\frac{1}{2}\hbar\omega_i(a,b) + k_{\mathrm{B}}T\ln\left(1 - e^{-\hbar\omega_i(a,b)/k_{\mathrm{B}}T}\right)\right]$$

HSE06 with room T vibrations predict phase boundary within 3% tensile strain in $MoTe_2$.

STRAIN INDUCED STRUCTURAL TRANSITION FROM 2H TO 1T'

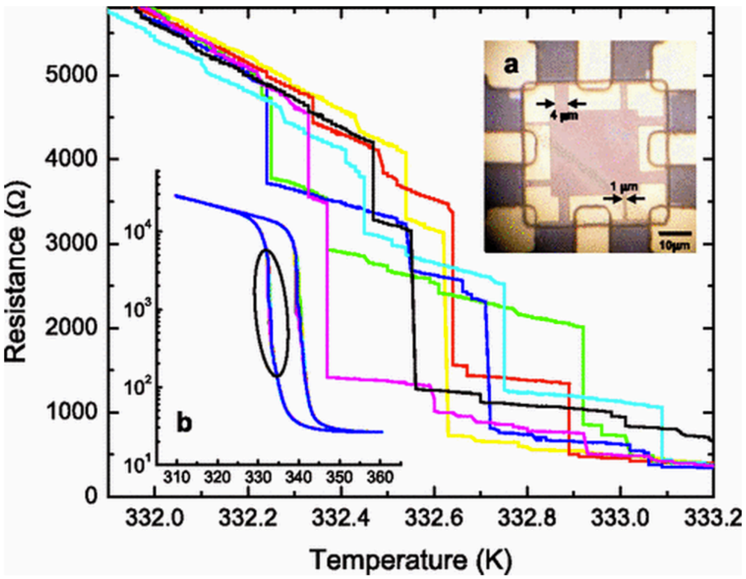


Duerloo, Li, Reed, Nature Communications, (2014).

CONTEXT: PHASE CHANGE MATERIALS FOR ELECTRONICS

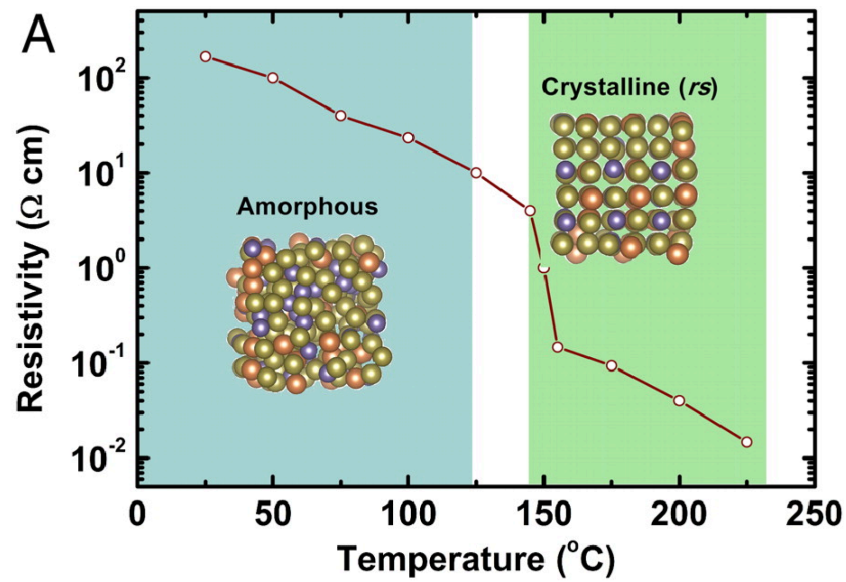
New materials are needed to mitigate escalating power requirements for electronic devices.

Metal-oxides: VO_2



Sharoni *et al. Phys. Rev. Lett.* **101**, 026404 (2008)

Chalcogenide alloys: $Ge_2Sb_2Te_5$ (GST)



Xu *et al.*, *PNAS*. **109**, 1055 (2012)

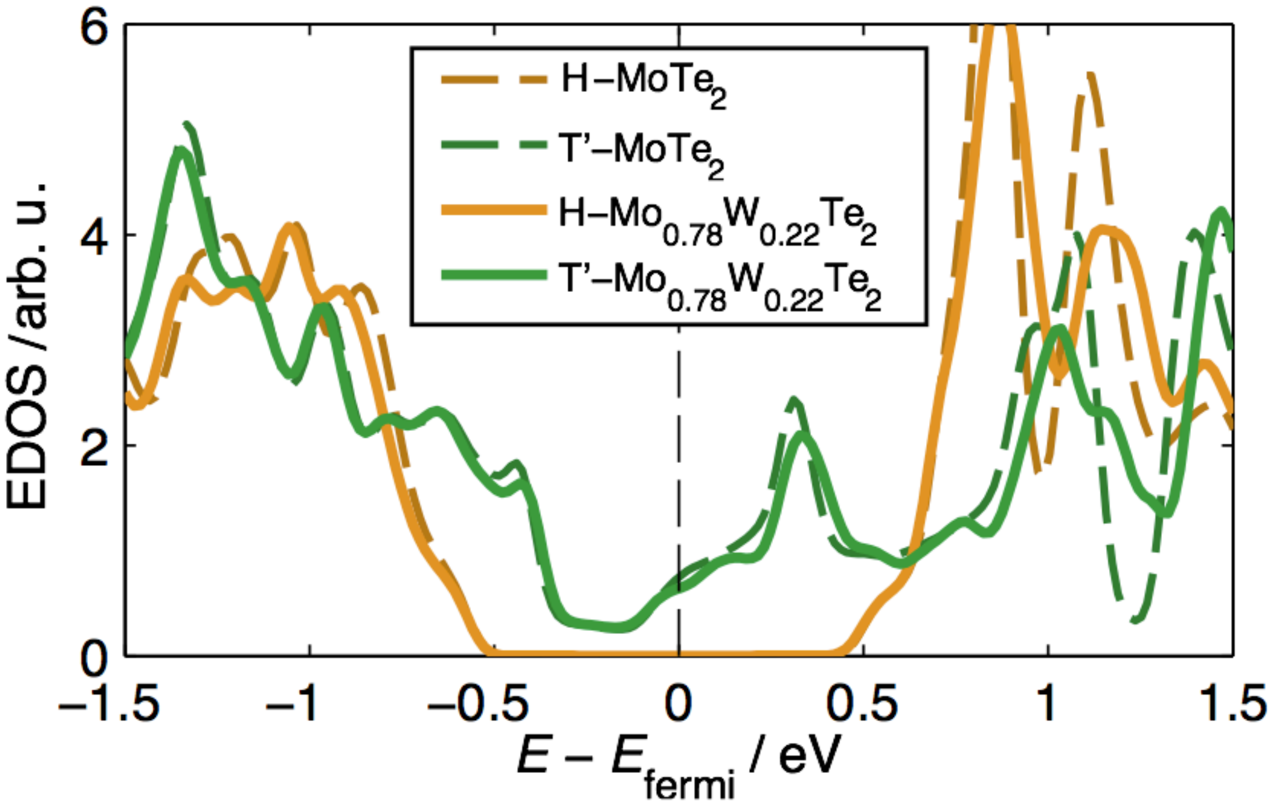
Suitable phase change materials are rare animals. We discover a promising new material.

Application spaces:

- Information and energy storage
- Low power electronics
- Infrared technologies

ELECTRONIC PROPERTIES DIFFER ACROSS PHASES

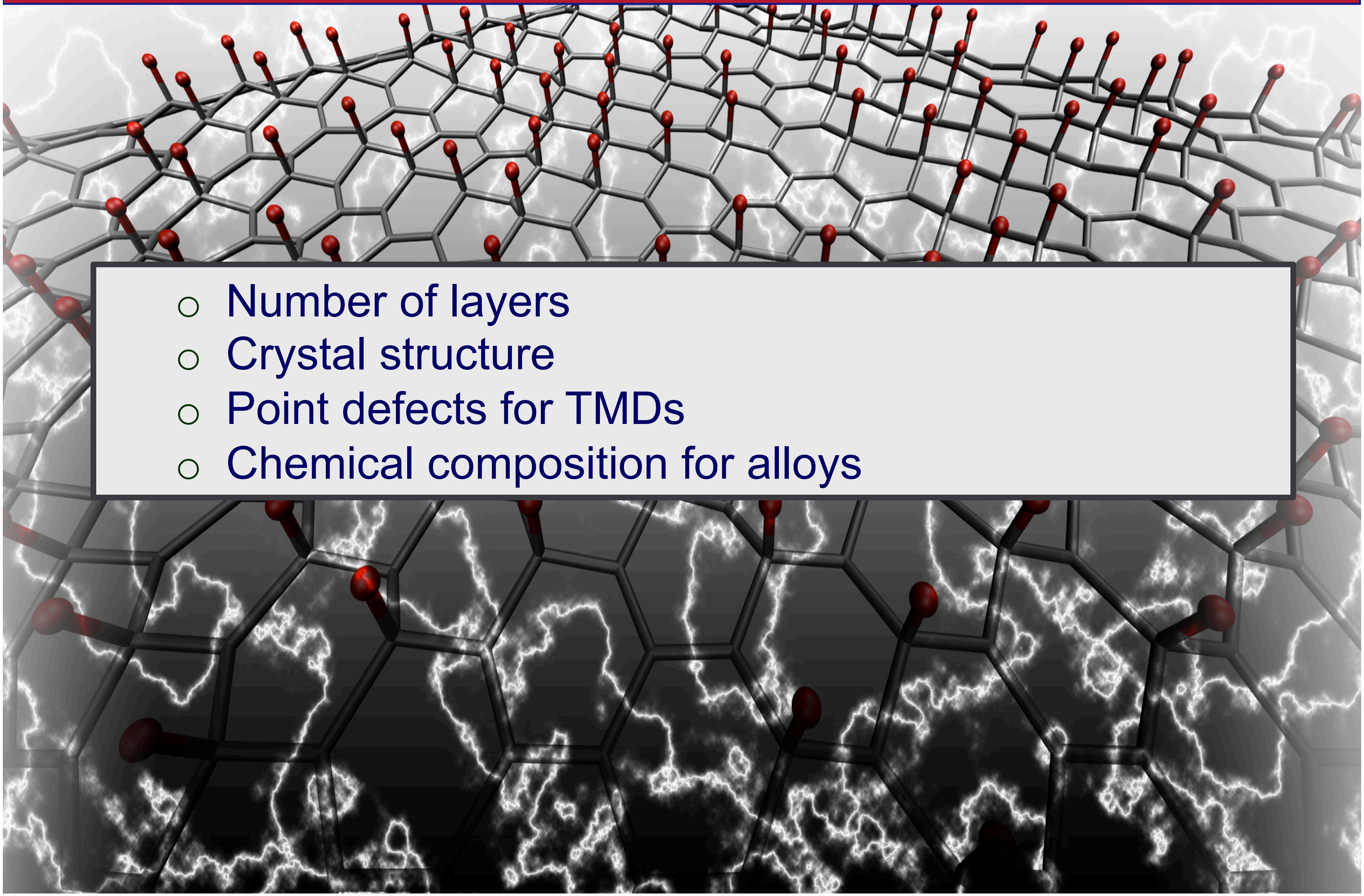
Kohn-Sham (single particle) electronic density of states for H and T' MoTe.



Large predicted electronic changes across the phase transition provide utility for electronic and infrared devices.

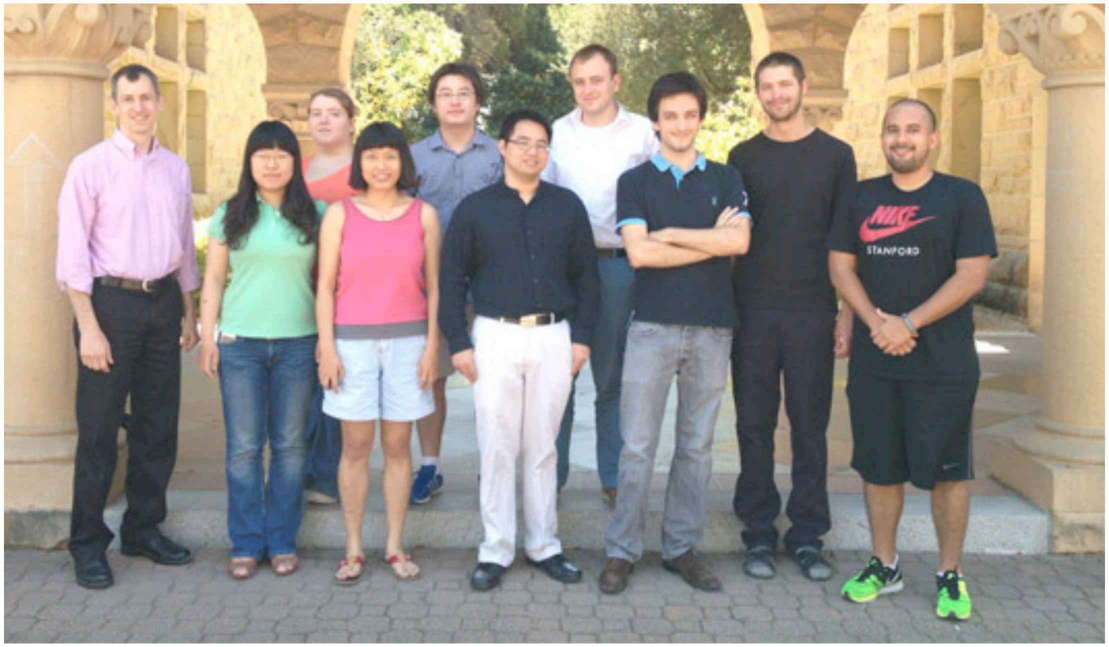
Duerloo, Reed, in review (2015).

METROLOGY NEEDS



- Number of layers
- Crystal structure
- Point defects for TMDs
- Chemical composition for alloys

ACKNOWLEDGEMENTS



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Mitchell Ong
Yao Li
Yao Zhou

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- National Energy Research Science Computing Center (NERSC)

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