DENSITY FUNCTIONAL THEORY CALCULATIONS FOR PHASE CHANGING MATERIALS:

BASIC CONCEPTS AND APPLICATIONS

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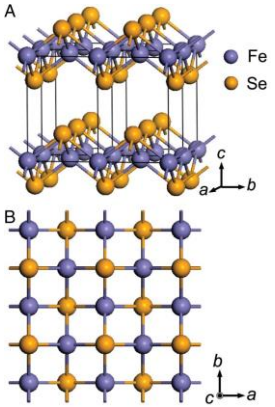
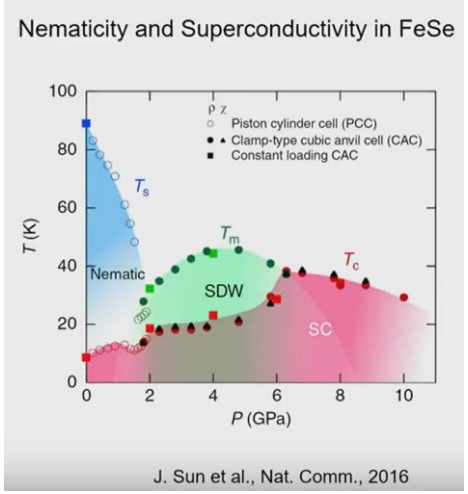
INFLUENCE OF A SYMMETRY-BREAKING STRAIN FIELD ON PHASE TRANSITIONS - FeSe

- Application of strain is one of the effective ways to engineer the various properties of materials. Iron-based superconductors are suitable materials to study the strain dependence of physical properties because their high sensitivity to variations in the local crystal structure.
- Among iron-based superconductors, FeSe is prominent example of the interplay between superconductivity, magnetism, and electronic nematicity, which can be tuned both by chemical substitution and application of physical pressure.



F-C Hsu, PNAS,2008



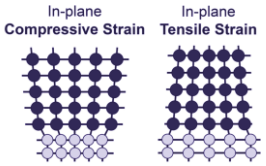
J. Sun et al., Nat. Comm., 2016

- Their electronic structures consist of multiple iron 3*d* orbitals, thus giving rise to a variety of antiferroic and ferroic ordering phenomena involving spin and orbital profiles. There has been increasing interest in nematic order which spontaneously breaks the rotational symmetry of electrons and triggers a lattice instability
- A structural transition from the parent tetragonal (P4/nmm, No. 129) crystal structure to the orthorhombic Cmma (No. 67) space group occurring at a temperature Ts ≈ 90 K is considered to be driven by electronic degrees of freedom and hence is referred to as a nematic transition.

http://strainedfesc.ipb.ac.rs/

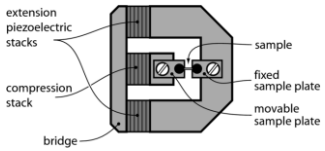
HOW TO STRAIN SINGLE CRYSTAL?

Lattice mismatch



During epitaxial growth, an epilayer monocrystalline material is grown on top of a substrate monocrystalline material. The periodicity of the substrate material provides a template for the epilayer material, but due to varying lattice parameters between the two materials, residual misfit strain is formed in the epilayer following coherent growth.

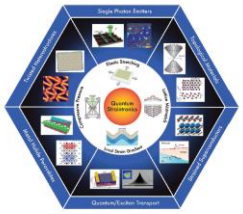
Piezoelectricity-based devices



The piezoelectricity-based devices for applying continuously tunable uniaxial strain have been made and successfully used in combination with different experimental techniques, in a wide temperature range, including cryogenic temperatures. The apparatus is compact and compatible with a wide variety of experimental probes.

C. W. Hicks et al. Rev. Sci. Instrum. 85, 065003 (2014)

Thin films and 2D materials



Elastic substrate ((PMMA),polyethylene terephthalate (PET),polyethylene naphtalate (PEN), polycarbonate (PC)

Local strain gradient (AFM tip, bubbles, nanopillars, wrinkles…)

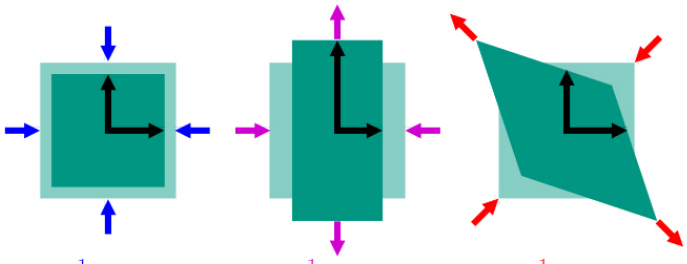
Compressive pressure (diamond anvil cell)

Thermal expansion between substrate and supported material.

Kim, J. M et al. *Adv. Mater.* 2022, 2107362

APPLICATION OF STRAIN

- Nematic order in the iron-based superconductors is closely tied to a lattice distortion and a structural transition. Applying stress in proper symmetry channels allows one to tune the nematic phase transition. The strong sensitivity to antisymmetric strain is a consequence of the anisotropic nature of the magnetic excitation spectrum.



crystallographic axes	Symmetry sector		
$e_x = (100), e_y = (010)$	$\varepsilon_{A_{1g}}$	$\varepsilon_{B_{2g}}$	$\varepsilon_{B_{1g}}$
$e_x = (110), e_y = (-110)$	$\varepsilon_{A_{1g}}$	$\varepsilon_{B_{1g}}$	$\varepsilon_{B_{2g}}$

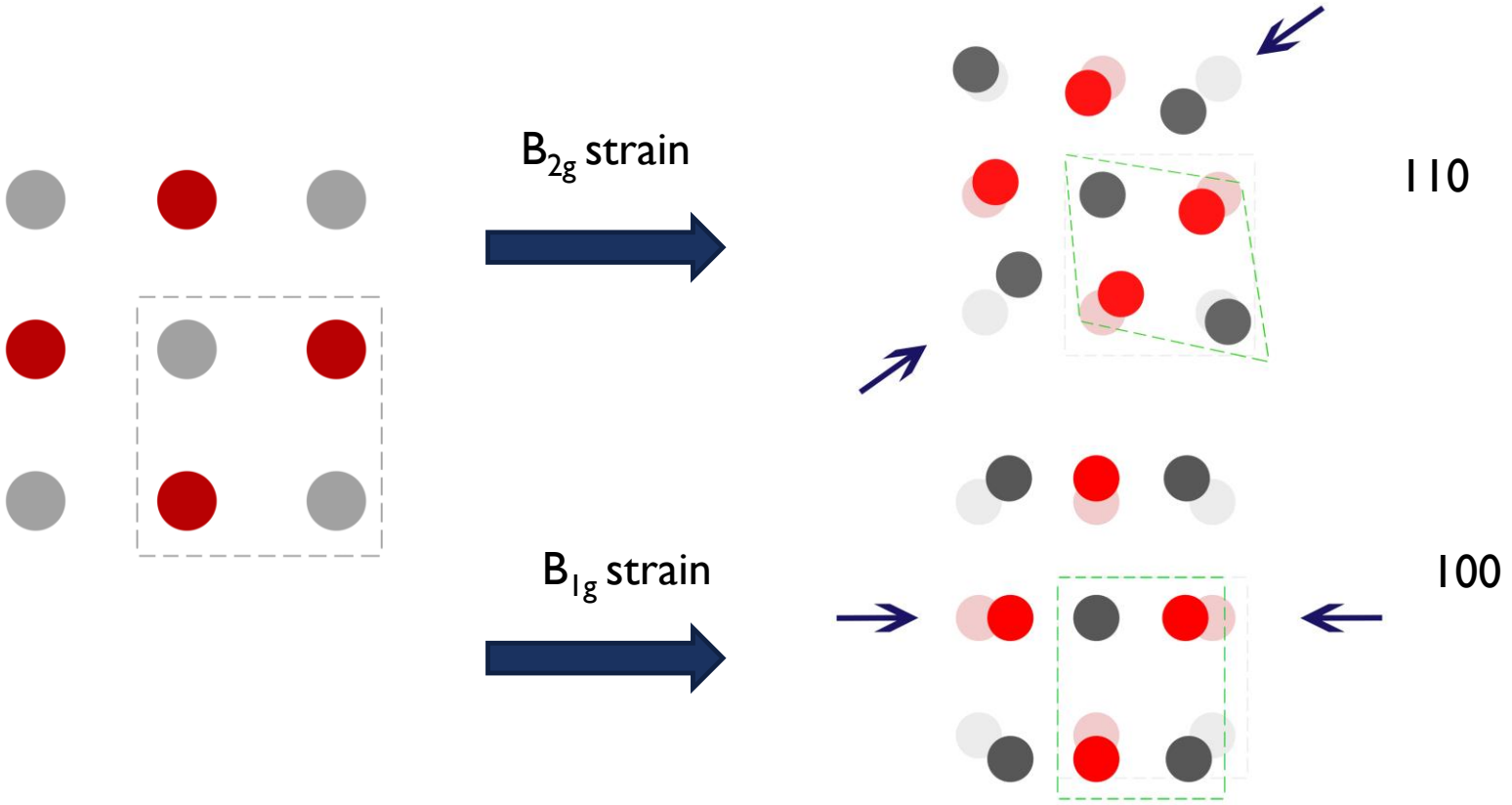
The channels A1g and B2g preserve the nematic axes (black), the B1g strain acts as a conjugate field, lifting the nematic degeneracy.

For the symmetry channel B2g, it is found a strong suppression of the nematic transition temperature occurs.

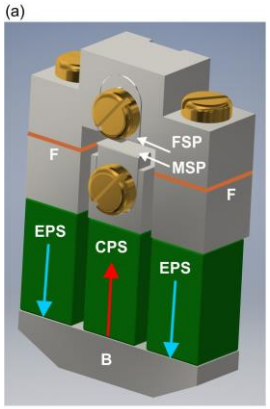
The degeneracy-lifting B1g strain is expected to act as an effective source field, replacing the nematic transition by a smooth crossover. In contrast, the symmetry-conserving strains of A1g and B2g types preserve the transition and merely yield a shift in the transition temperature.

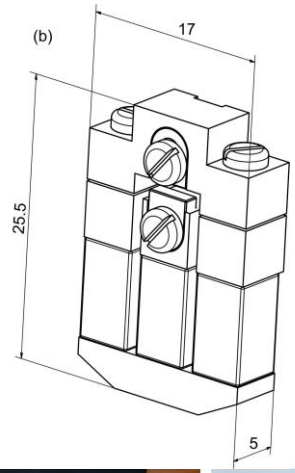
Willa, R., Fritz, M., & Schmalian, J. (2019). *Strain tuning and anisotropic spin correlations in iron-based systems. Physical Review B, 100(8)*

FESE UNDER STRAIN

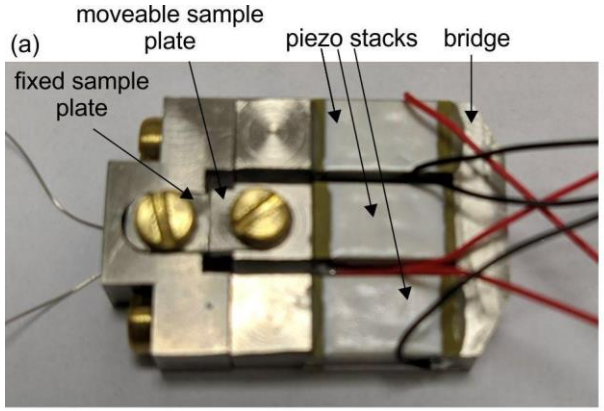


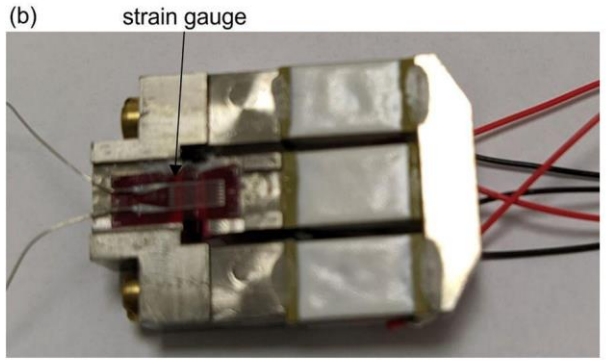
EXPERIMENTAL SETUP - STRAINED FESC

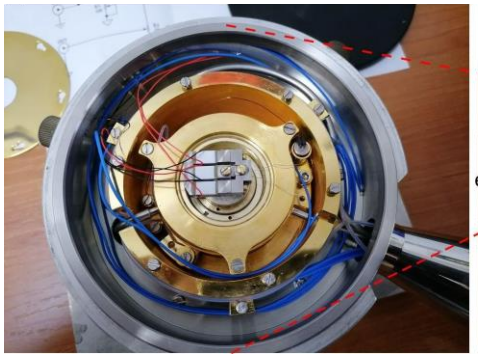


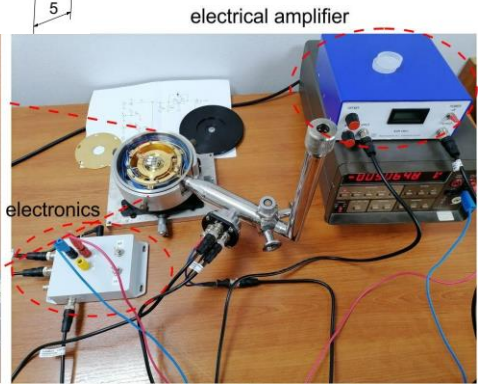


In order to perform inelastic light scattering studies and scanning probe microscopy based experiments of samples under uniaxial strain, within Strained FeSC project we designed, developed and fabricated a piezoelectric-based device.



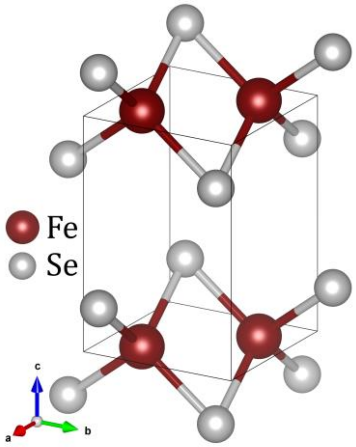






[1] C. W. Hicks et al. "Piezoelectric-based apparatus for strain tuning", Rev. Sci. Instrum. 85, 065003 (2014)
[2] J. Schmidt et al. Nematicity in the superconducting mixed state of strain detwinned underdoped Ba(Fe1−xCox)2As2 , Phys. Rev. B 99, 064515 (2019)

DFT CALCULATIONS



	-2.00%	-1.50%	-1.00%	-0.50%	0.00%	0.50%	1.00%	1.50%	2.00%
a	3.6953	3.7142	3.7330	3.7519	3.7707	3.7896	3.8084	3.8273	3.8461
b	3.7707	3.7707	3.7707	3.7707	3.7707	3.7707	3.7707	3.7707	3.7707
c	5.6328	5.6042	5.5759	5.5479	5.5202	5.4927	5.4655	5.4386	5.4119
Fe-Se (‖*a*)	2.3828	2.3854	2.3880	2.3907	2.3935	2.3965	2.3995	2.4026	2.4059
Fe-Se (‖*b*)	2.4122	2.4074	2.4027	2.39811	2.3935	2.3890	2.3846	2.3802	2.3758
Fe-Fe	2.6398	2.6464	2.6530	2.65964	2.6663	2.6730	2.6797	2.6864	2.6931

No relaxation!
The Se position, above the Fe plane, significantly shorter for the relaxed structure, for almost 10% as compared with the experimental one. It is found that electronic band structure, DOS and Fermi surface are found to be strongly dependent on the value of the height of Se atoms above Fe layers (J. Kumar et al. Supercond. Sci. Technol. **25**, 095002 (2012)).

We use the experimental parameters and the volume cell of the unit cell is conserved under applied uniaxial strain (as in M. Ghini et al. Phys. Rev. B 103, 205139 (2021))

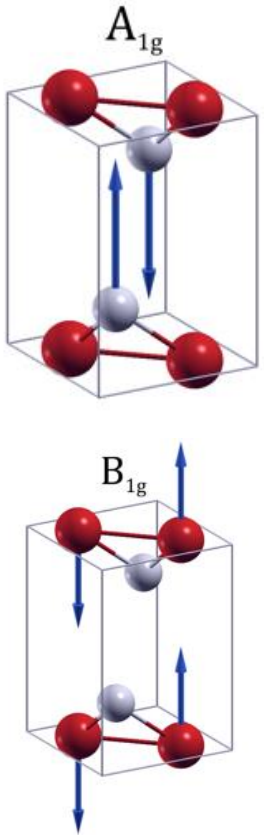
DFT CALCULATIONS

EXPERIMENTAL
A_{1g} = 180.71
B_{1g} = 204.44

CALCULATED
A_{1g} = 190.5
B_{1g} = 226.1

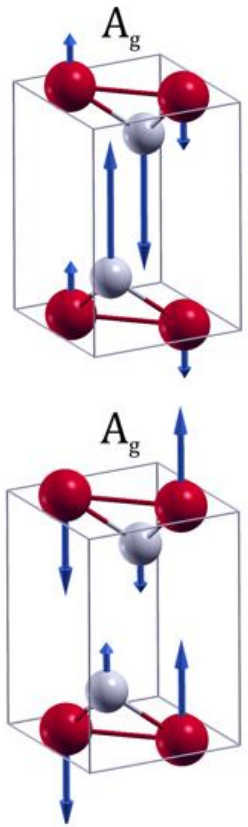
The A1g and B1g modes come from the vibrations of Se atoms along the c axis and the vibrations of Fe atoms along the c axis, respectively

Space group 129



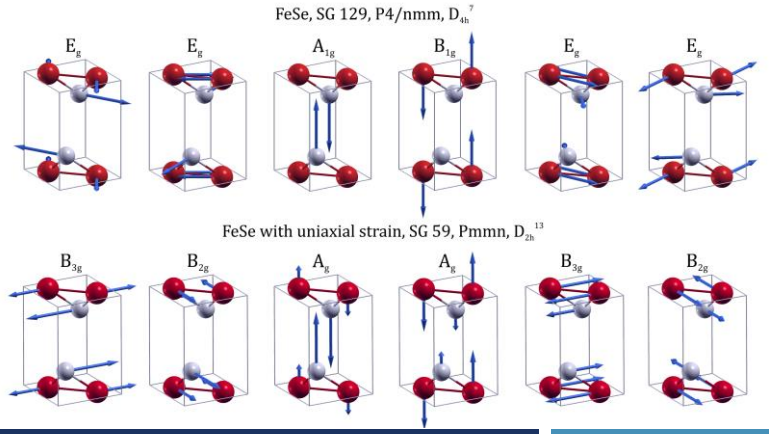
B_{1g} strain

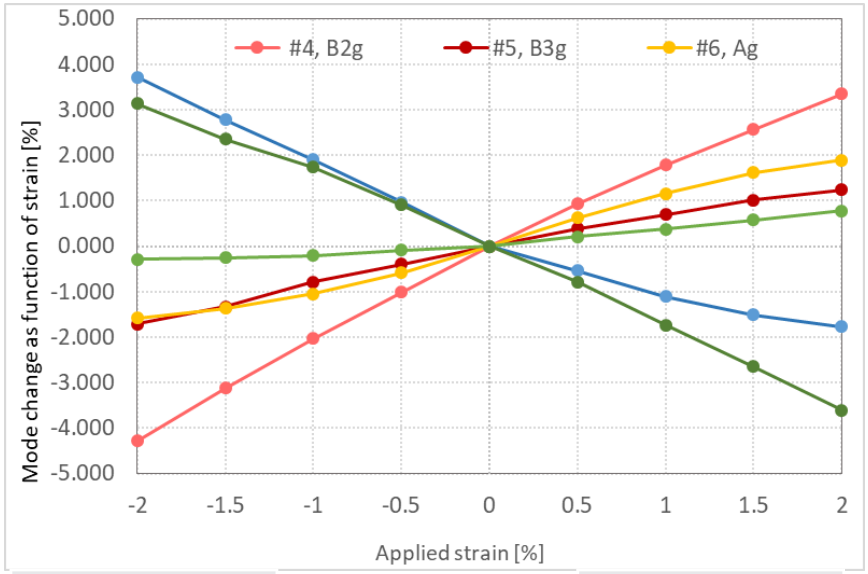
Space group 59



DFT CALCULATIONS

Mode old	4-5, Eg	4-5, Eg	6, A1g	7, B1g	10-11, Eg	10-11, Eg
Mode new	#4, B2g	#5, B3g	#6, Ag	#8, Ag	#10, B2g	#11, B3g
Strain (%)	Diff. (%)	Diff. (%)	Diff. (%)	Diff. (%)	Diff. (%)	Diff. (%)
-2	-4.280	-1.712	-1.575	3.715	-0.289	3.143
-1.5	-3.113	-1.323	-1.365	2.786	-0.248	2.357
-1	-2.023	-0.778	-1.050	1.902	-0.207	1.737
-0.5	-1.012	-0.389	-0.577	0.973	-0.083	0.910
0	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.934	0.389	0.630	-0.531	0.207	-0.786
1	1.790	0.700	1.155	-1.106	0.372	-1.737
1.5	2.568	1.012	1.627	-1.504	0.579	-2.647
2	3.346	1.245	1.890	-1.769	0.786	-3.598





A1g	
187.5	-2%
187.9	-1.5%
188.5	-1%
189.4	-0.5%
190.5	0%
191.7	0.5%
192.7	1%
193.6	1.5%
194.1	2%

B1g	
234.5	-2%
232.4	-1.5%
230.4	-1%
228.3	-0.5%
226.1	0%
224.9	0.5%
223.6	1%
222.7	1.5%
222.1	2%

ACKNOWLEDGEMENT

- PHEMTRONICS project for inviting me to make this lecture at "European School on Plasmonics and Phase Change Materials "

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- DFT calculations were performed using computational resources at Johannes Kepler University (Linz, Austria) and with local resources at IPB

THANK YOU ALL FOR YOUR ATTENTION