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Transient Enhancement of the Ferroelectricity in the Rashba Semiconductor α-GeTe

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Introduction and motivation

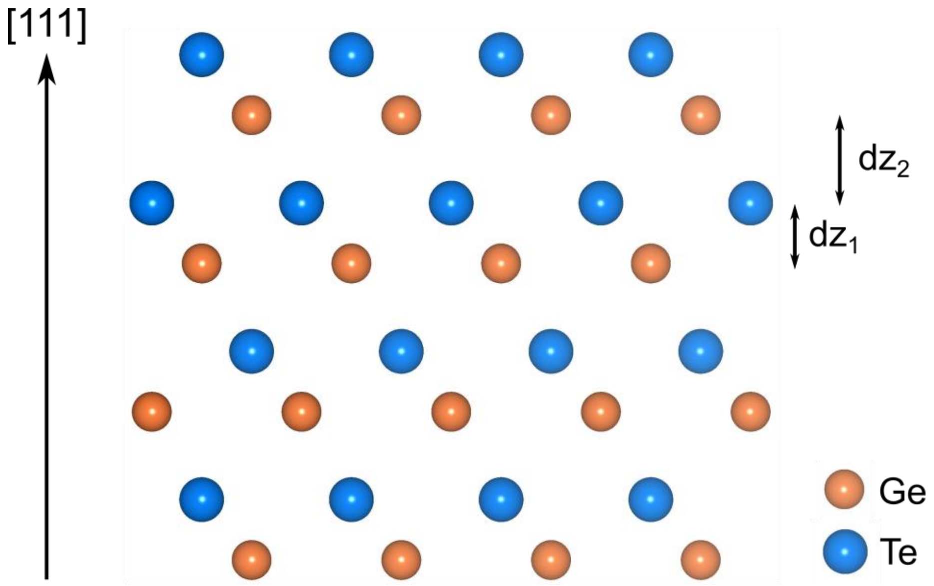
Introduction

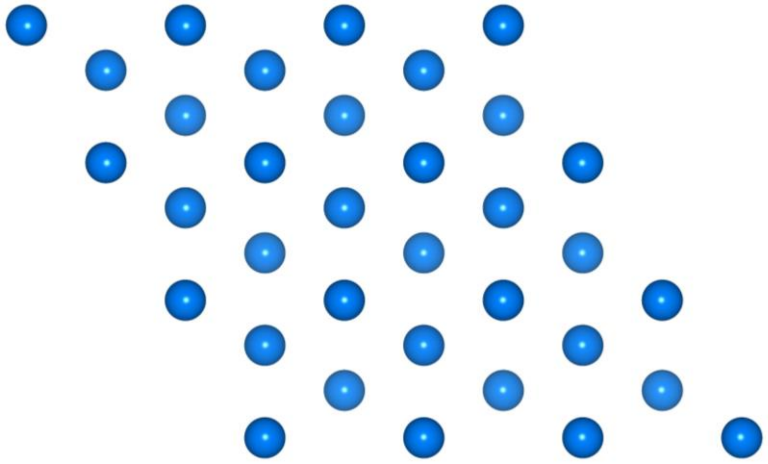
Germanium telluride is a semiconducting and ferroelectric material at RT

Below the Curie temperature (700 K), GeTe adopts a rhombohedral structure

The strong lattice distorsion ($dz_2 > dz_1$) along the 111 direction leads to the ferroelectric order

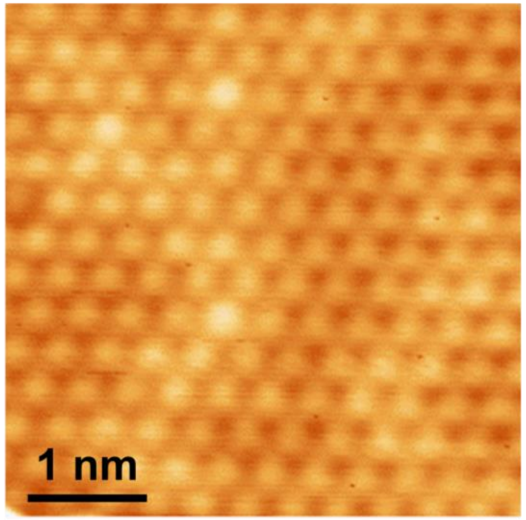
High-quality α-GeTe(111) can be epitaxially grown by MBE with Te termination





Top view

STM α-GeTe(111)



G. Kremer et al., PRR **2**, 033115 (2020)

Rashba effect

Inversion symmetry

$$E(k,\uparrow) = E(-k,\uparrow)$$

Time-reversal symmetry

$$E(k,\uparrow) = E(-k,\downarrow)$$

→ Spin degenerate

$$E(k,\uparrow) = E(k,\downarrow)$$

~~**Inversion symmetry**~~

~~$$E(k,\uparrow) = E(-k,\uparrow)$$~~

Time-reversal symmetry

$$E(k,\uparrow) = E(-k,\downarrow)$$

→ Spin split

$$E(k,\uparrow) \neq E(k,\downarrow)$$

For a 2D electron gas: Rashba Hamiltonian

$$H_{eff} = H_0 + H_{SO}$$

$$H_0 = -\frac{\hbar^2}{2m}\vec{\nabla}^2$$

$$H_{SO} = \frac{\hbar}{4m^2c^2}(\vec{\nabla}V \times \vec{p}) . \vec{s}$$

k dependent splitting

$$E_{\pm}(k) = \frac{\hbar^2 k^2}{2m} \pm \alpha_R k$$

α_R:

- Spin-orbit strength
- Surface gradient potential

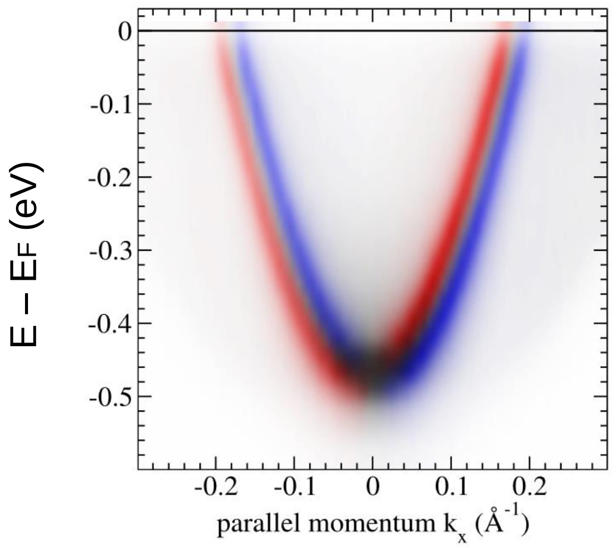
Rashba systems measured by ARPES

(i) **Surface states of metals**: invertion symmetry is broken due to the existence of the surface (As(111), Au(111), Cu(111) …)

(ii) **Bulk states**: non-centrosymmetric semiconductors with a polar structure and a large spin-orbit interaction (BiTeBr, BiTeI, BiTeCl)

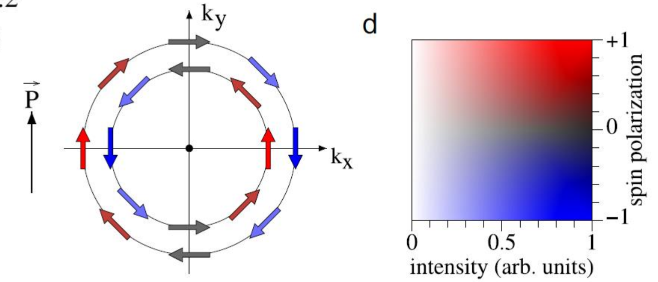
Au(111)

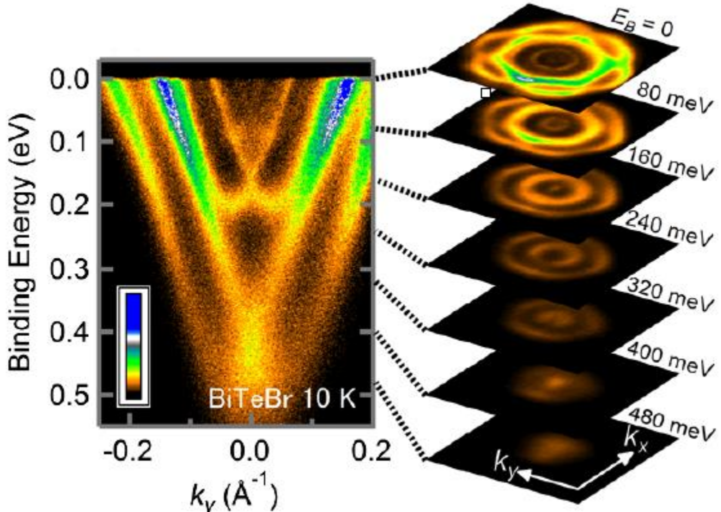
C. Tusche et al., Ultramicroscopy 159 (2015) 520–529



E – EF (eV)

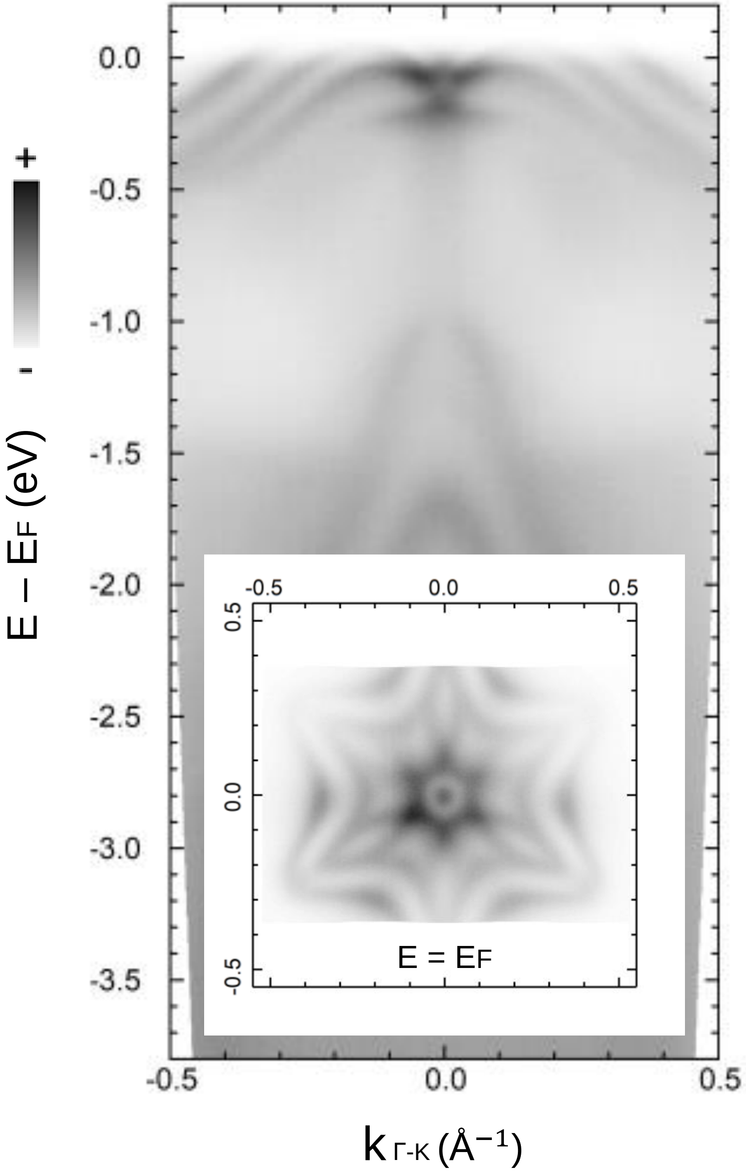
Spin-momentum locking



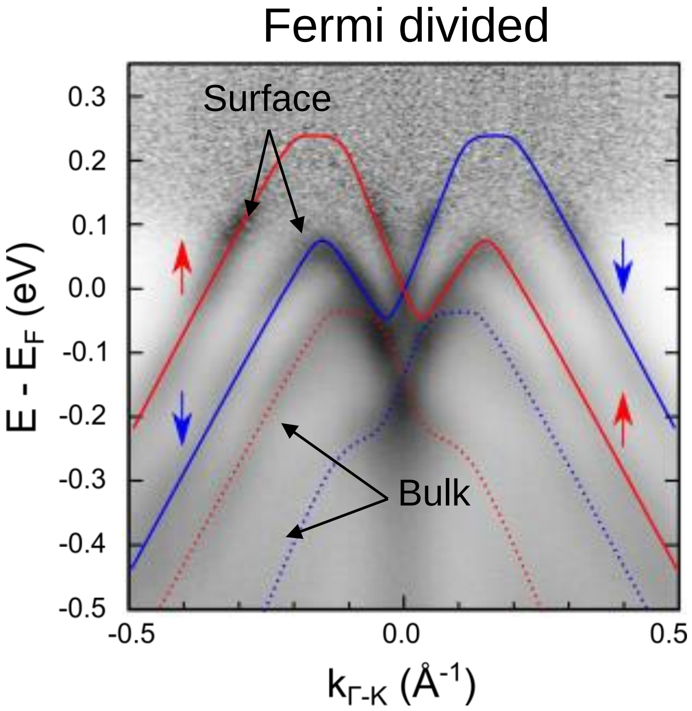


M. Sakano et al., Phys. Rev. Lett. **110**, 107204 (2013)

GeTe : a ferroelectric Rashba semiconductor



ARPES on K doped α-GeTe(111) at 300 K and with 21.2 eV



G. Kremer et al., PRR **2**, 033115 (2020)

Symmetry breaking along the (111) direction and spin-orbit interaction gives rise to :

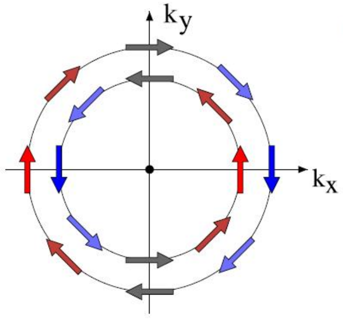
- Giant **bulk** Rashba effect
- Spin polarized surface and bulk states with a large splitting as probed by (SR-)ARPES
- Possible to manipulate / reverse the ferroelectricity using an external electric field : see J. Krempasky et al., PRX **8**, 021067 (2018)

Ferroelectric Rashba semiconductor

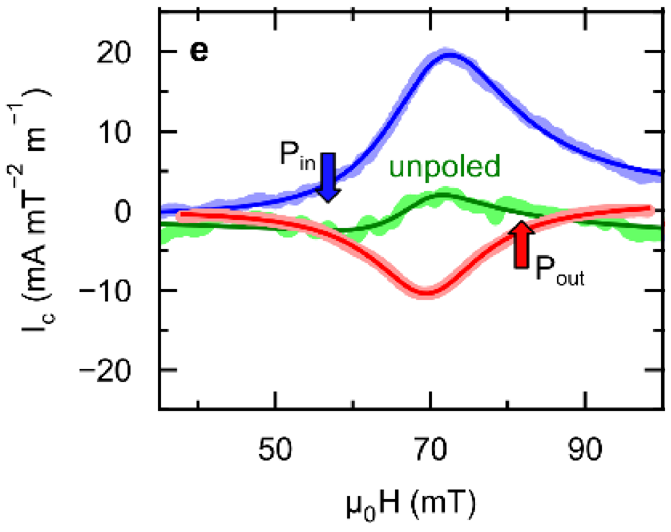
Spin-to-charge conversion in GeTe

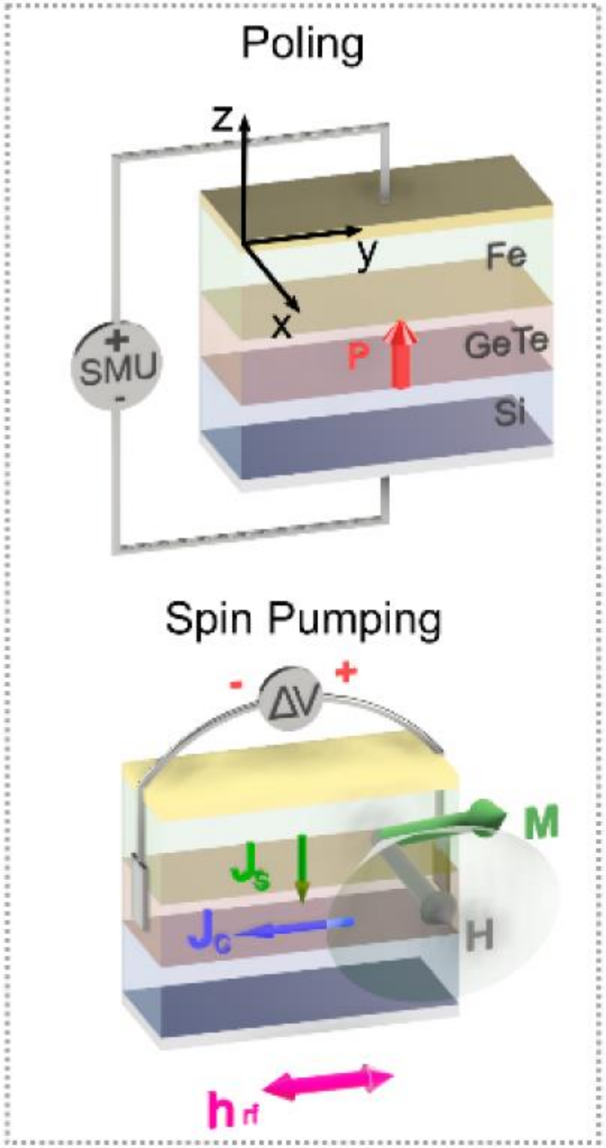
GeTe: ferroelectric Rashba semiconductor

- Rashba: spin-momentum locking
- Ferroelectric:
  - non-volatile effect
  - electric control of polarization $\vec{P}$ (SMU)



$\vec{J_C}$ along high symmetry direction



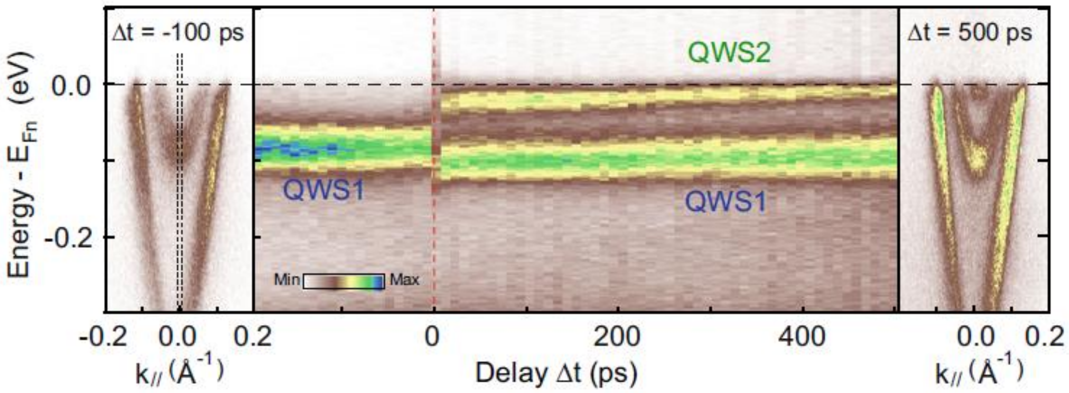


Generation of spin current $\vec{J_S}$ by microwave field and staturating field $\vec{H}$

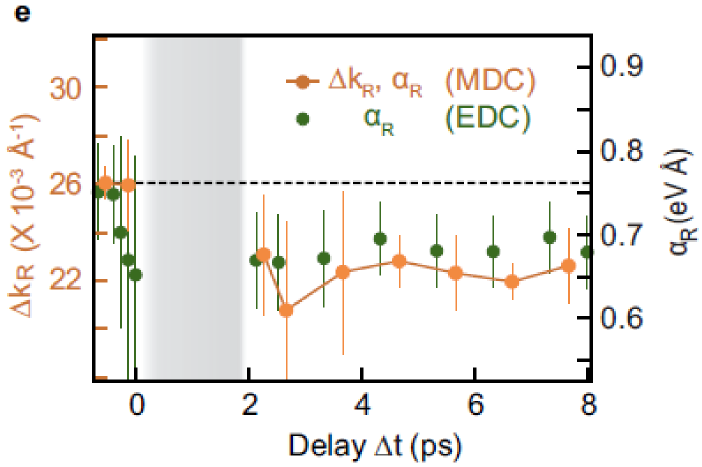
Varotto *et al.*, Nature Electronics (2021)

Optical manipulation of Rashba-split 2-dimensional electron gas on K-doped Bi_2Se_3

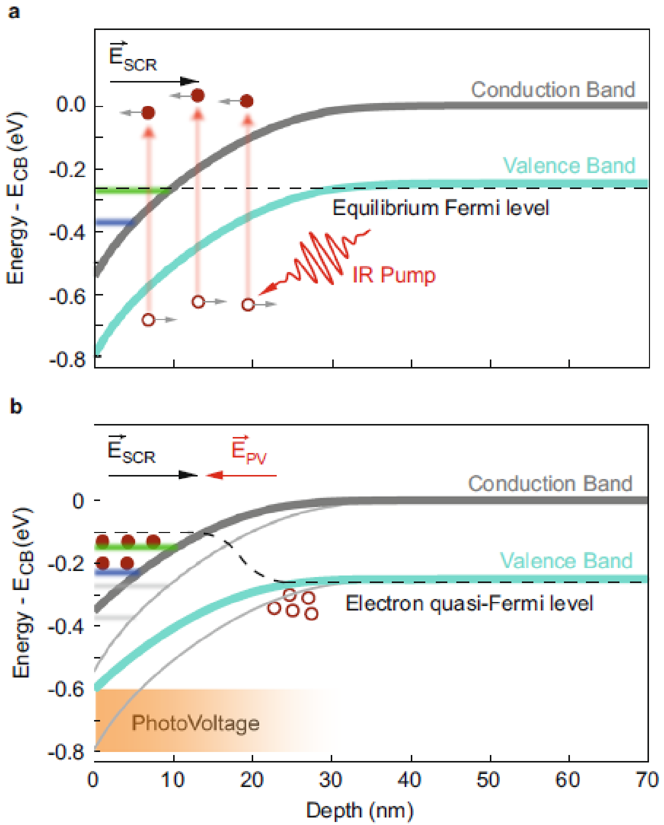
K-doped Bi_2Se_3 is a semiconductor with a significant band bending.



In few picosecond, the Rashba splitting of the 2DEG is reduced by ~20%.



$$E_{\pm}(k) = \frac{\hbar^2 k^2}{2m} \pm \alpha_R k$$



This is explained as the consequence of Surface Photovoltage (SPV) reducing the surface confining potential.

⟹ weaker Rashba splitting

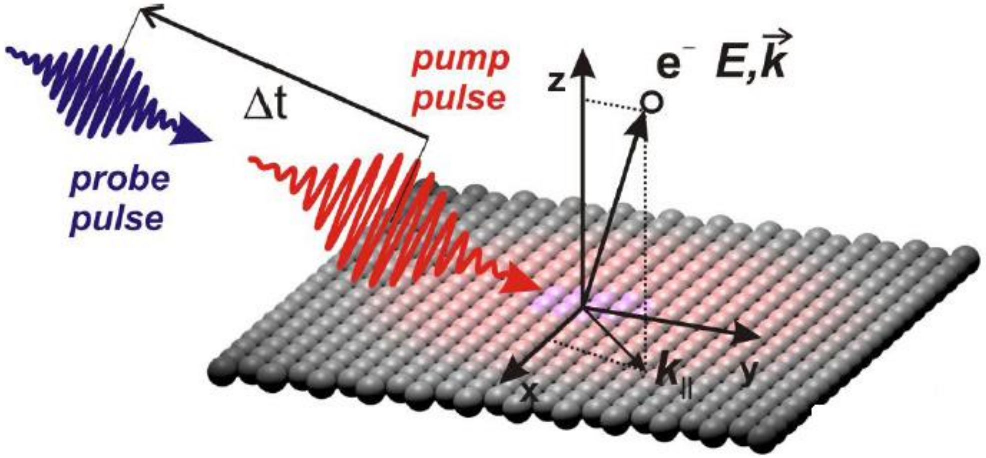
Michiardi *et al.*, Nature Commun. 2022

Motivation : out-of-equilibrium dynamics of GeTe

Is optical control of the ferroelectricity in GeTe possible?
It could be interesting for applications in spintronics!

- Can we control the Rashba splitting of GeTe with an femtosecond optical pulse?
- Semiconductor: a surface photovoltage can be induced! How strong?
- How does the electronic structure evolve on the ps timescale ?

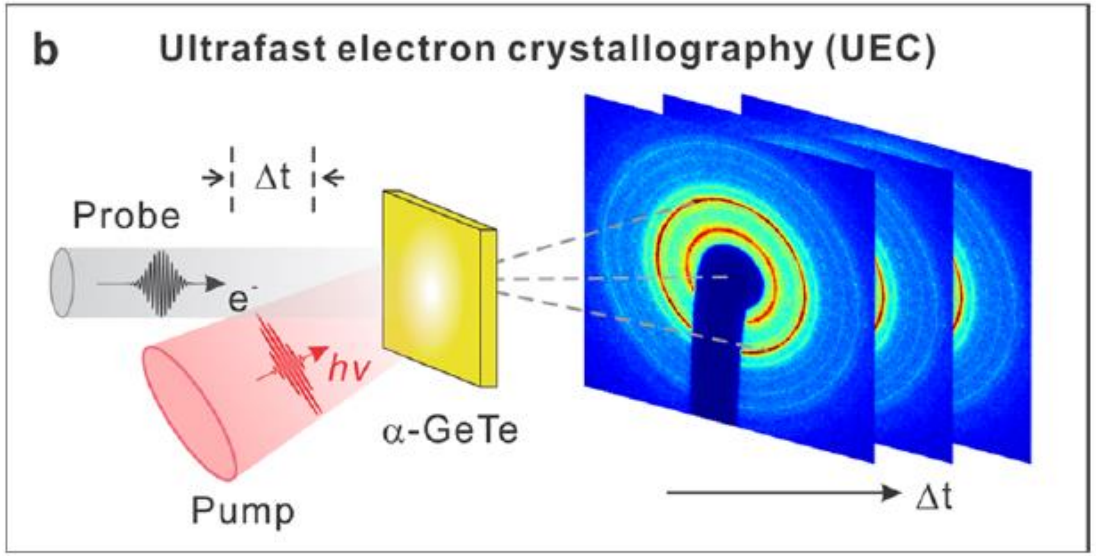
➢ The ideal technique to answer these questions is time-resolved ARPES

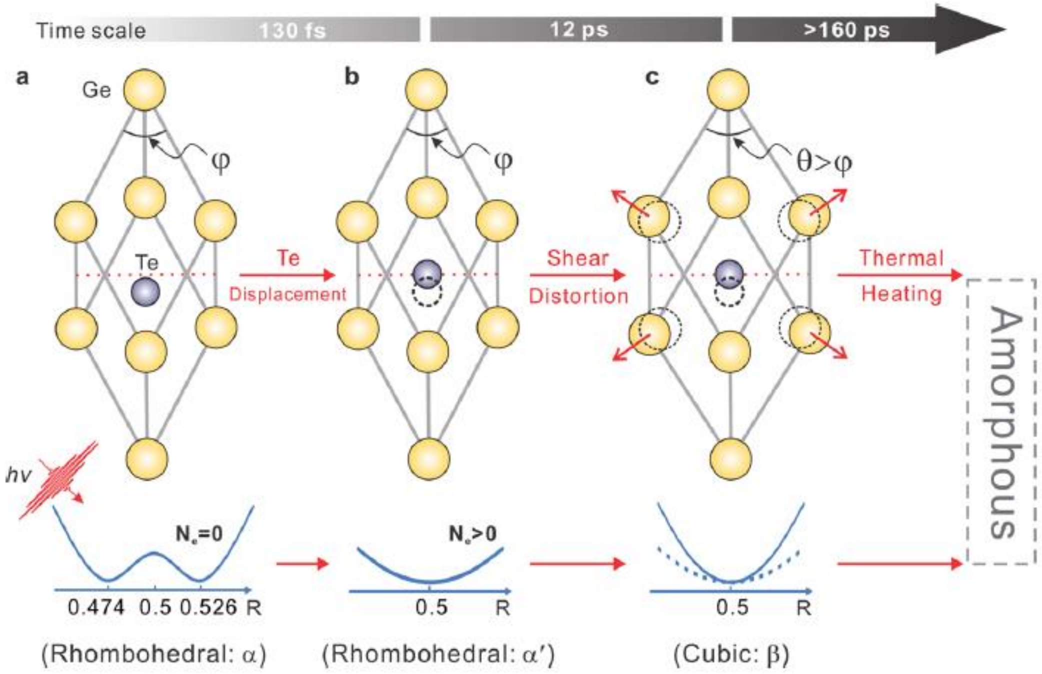


Out-of-equilibrium dynamics of GeTe?

Previous works:

- ❑ Ultrafast electron diffraction of GeTe (transmission)
  - on a 20 nm thin film
  - 800 nm pump with > 1 mJ/cm^2





J. Hu *et al.*, ACS Nano 2015

Transition from ferroelectric phase to paraelectric state in less than 1 ps.

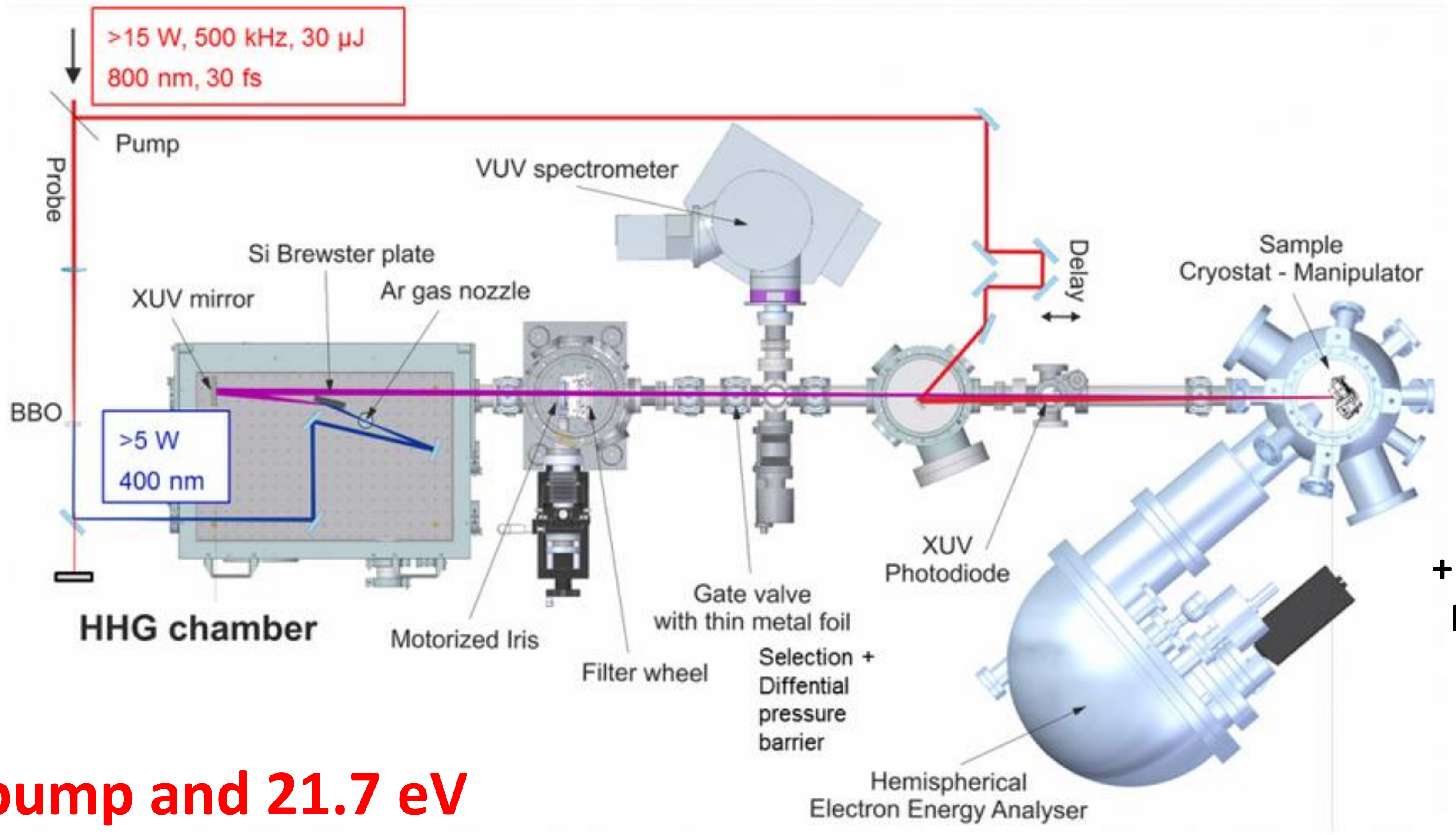
- ❑ TD-DFT MD simulation confirms the dynamics (Wang *et al.*, PRL 120, 185701 (2020))

XUV trARPES experimental setup

FRITZ HABER INSTITUTE
DEPT. OF PHYSICAL CHEMISTRY
MAX PLANCK SOCIETY

For more details, see :
M. Puppin et al., Rev. Sci. Instrum. **90**, 023104 (2019)

Rep. Rat : 500 kHz
Energy res. : 121 meV
Time res. : 37 fs



trARPES_setup

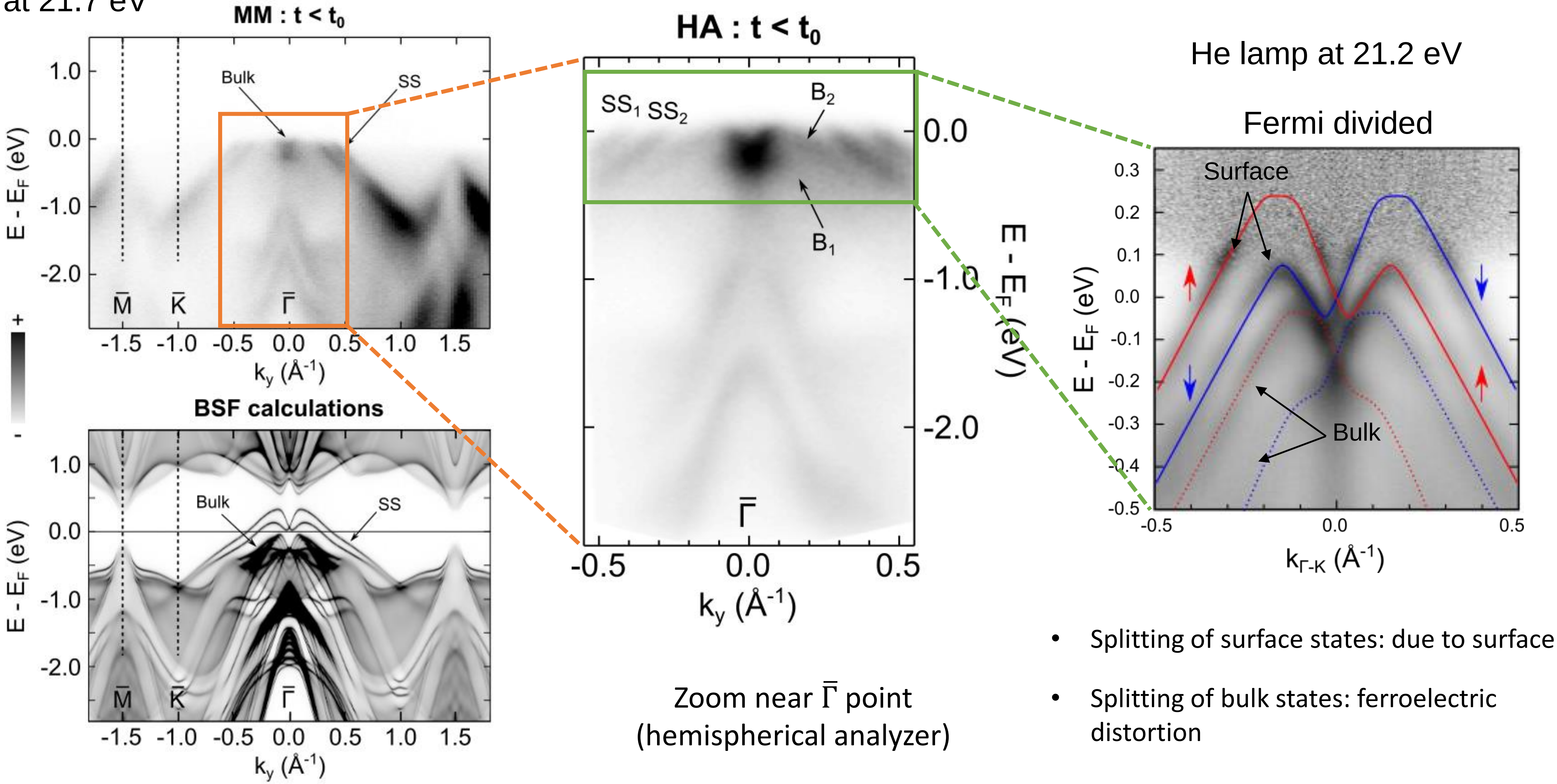
+ Momentum Microscope

We used 1.55 eV pump and 21.7 eV probe during our measurements

Results

Low-energy electronic structure of GeTe at FHI

Laser at 21.7 eV

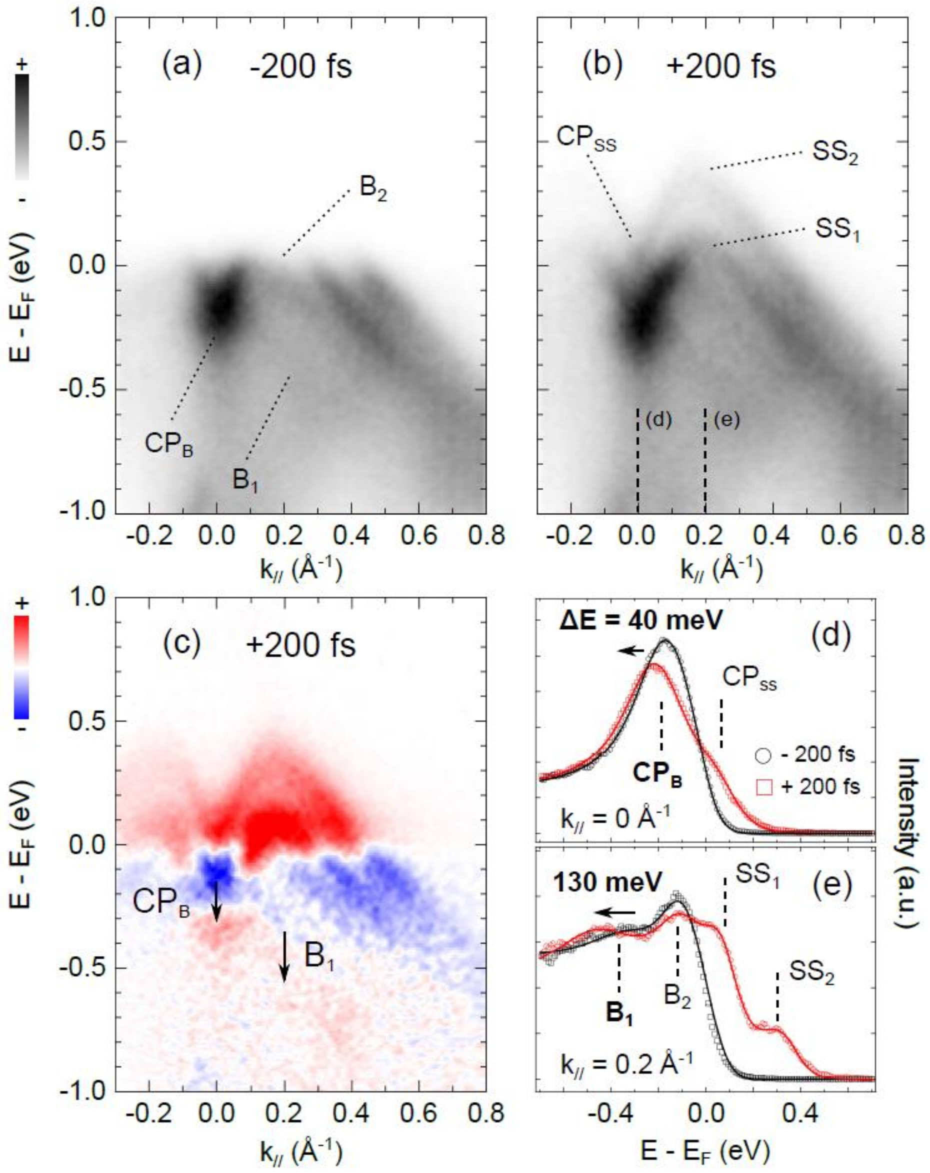


Zoom near $\bar{\Gamma}$ point (hemispherical analyzer)

- Splitting of surface states: due to surface
- Splitting of bulk states: ferroelectric distortion

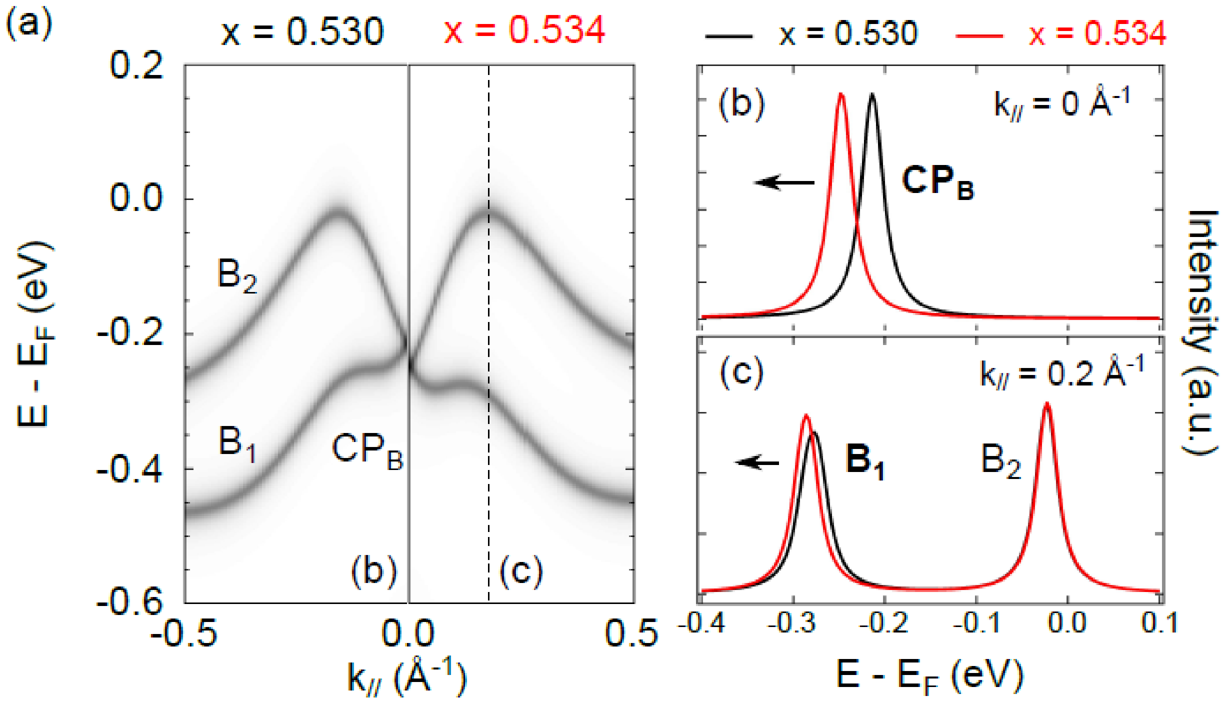
With the momentum microscope (TOF): full Brillouin zone

Dynamics of states at $\bar{\Gamma}$: ferroelectricity increase!



More interesting dynamics of bulk states B_1 and B_2!

- Transient shift of B_1 to higher binding energy
- The Rashba splitting of the bulk states increases!



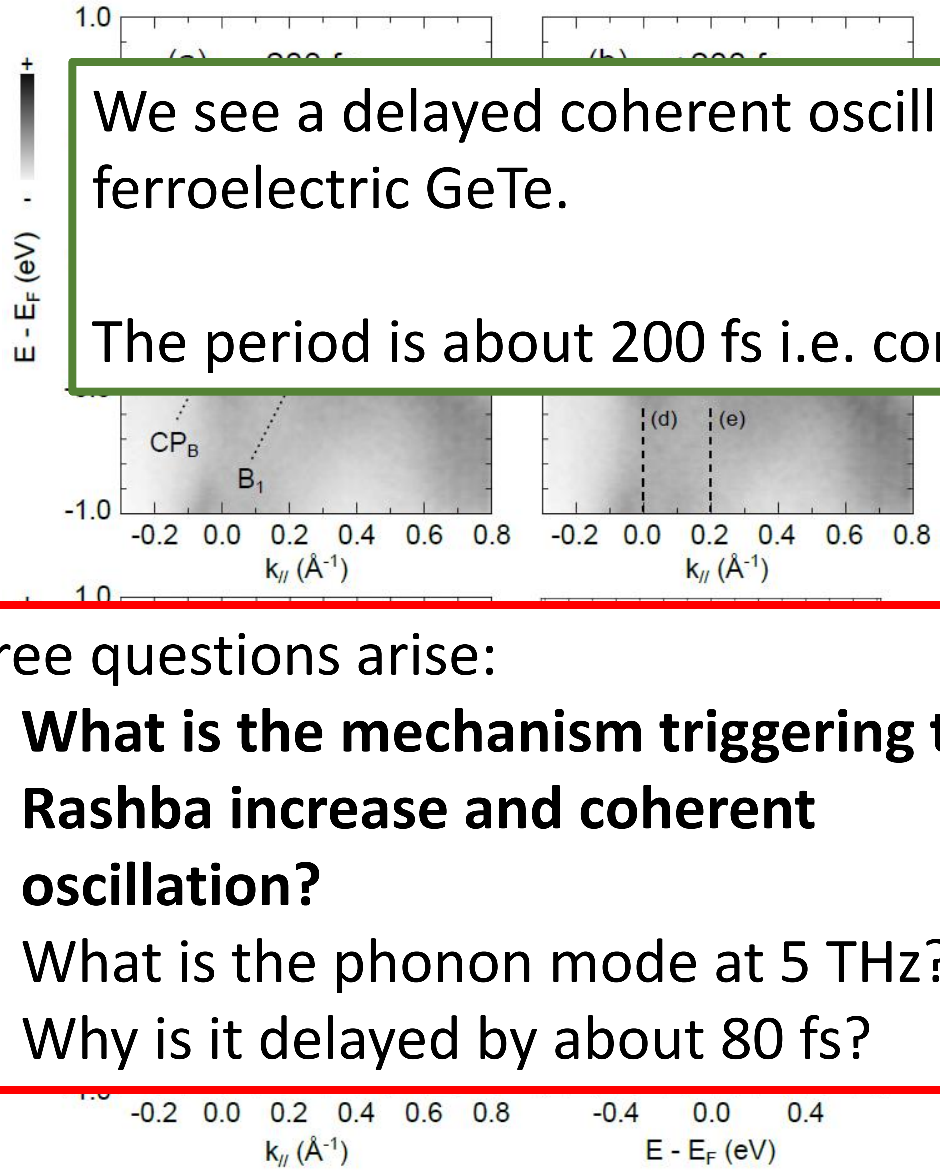
- Can be reproduced by an increase of the ferroelectric distortion!

Dynamics of states at $\bar{\Gamma}$: transient ferroelectricity modulation

More interesting dynamics of bulk states B1 and B2!

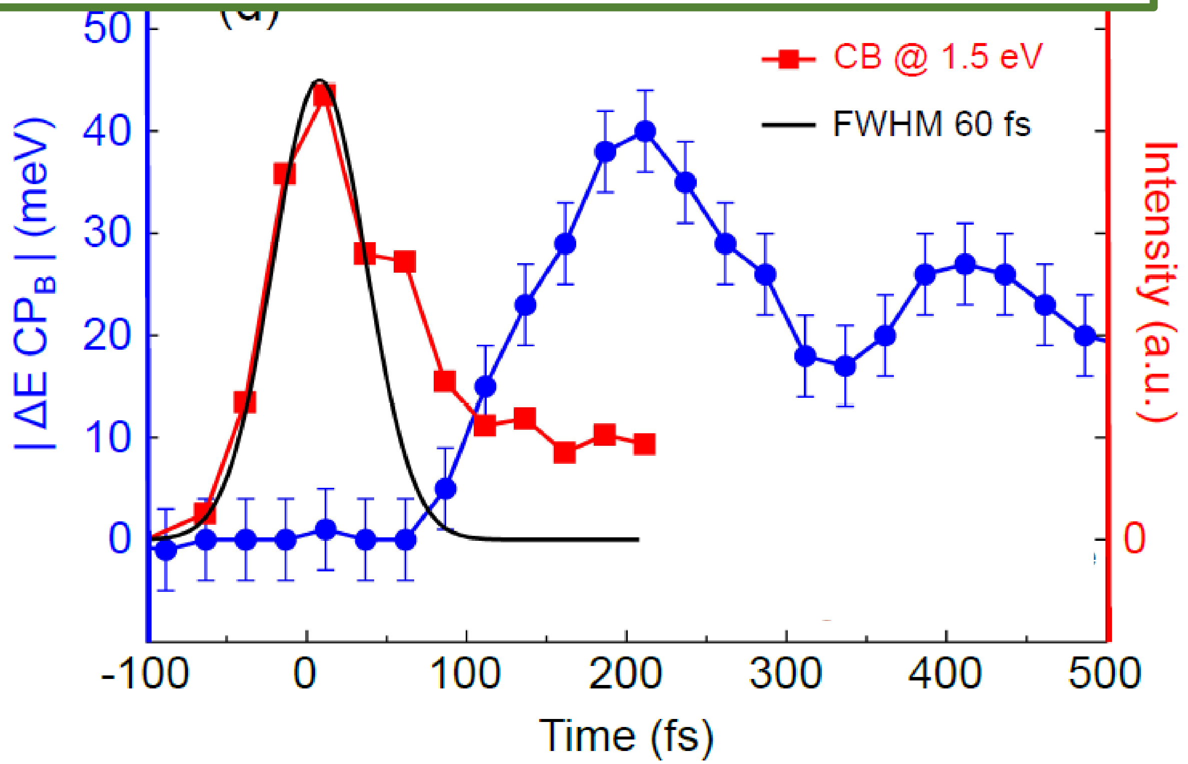
We see a delayed coherent oscillation of the Rashba splitting at the surface of ferroelectric GeTe.

The period is about 200 fs i.e. corresponds to a frequency of 5 THz.



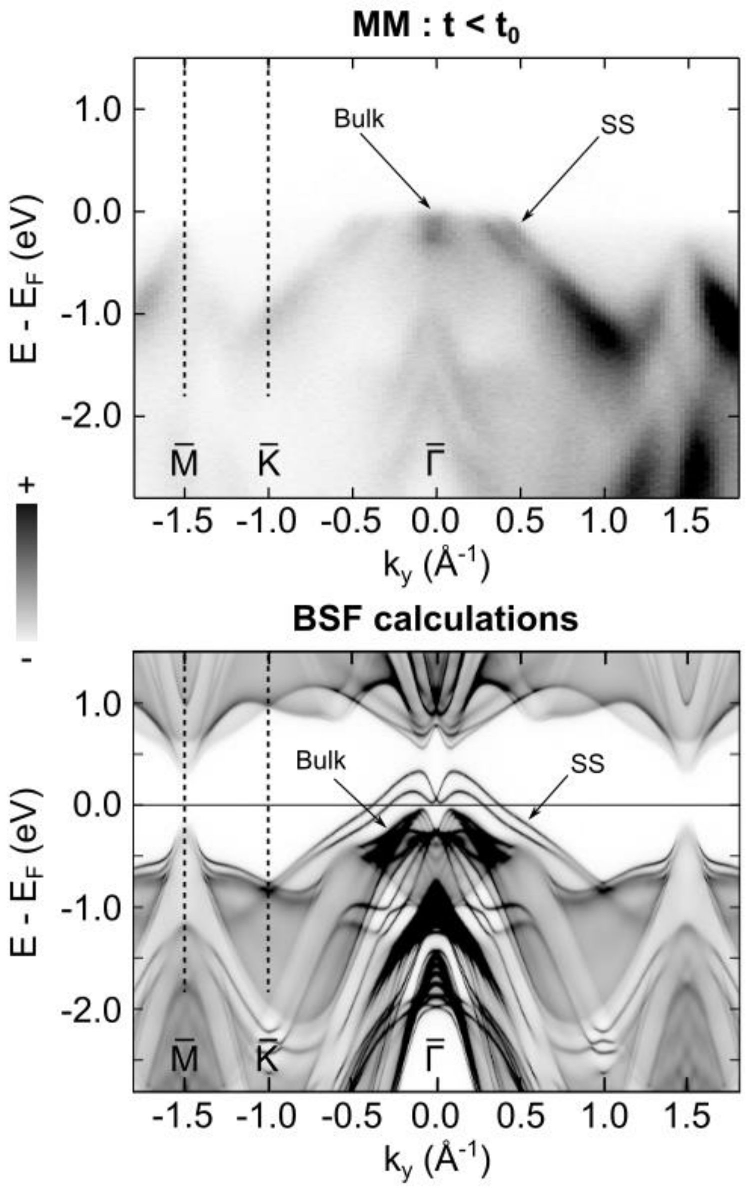
Three questions arise:

1. **What is the mechanism triggering the Rashba increase and coherent oscillation?**
2. What is the phonon mode at 5 THz?
3. Why is it delayed by about 80 fs?



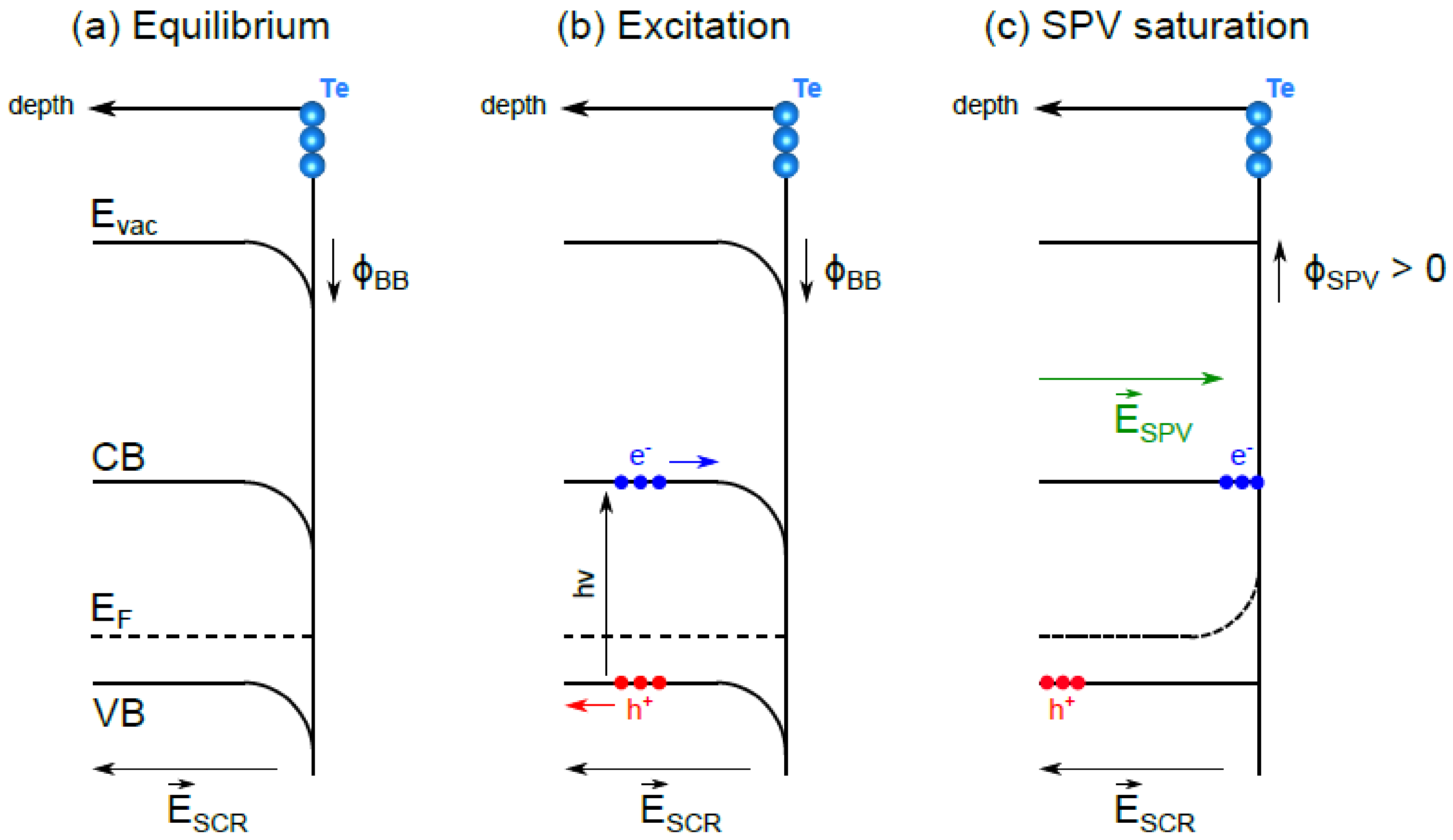
Blue: transient evolution of the energy shift of CPB

Transient ferroelectricity increase: origin



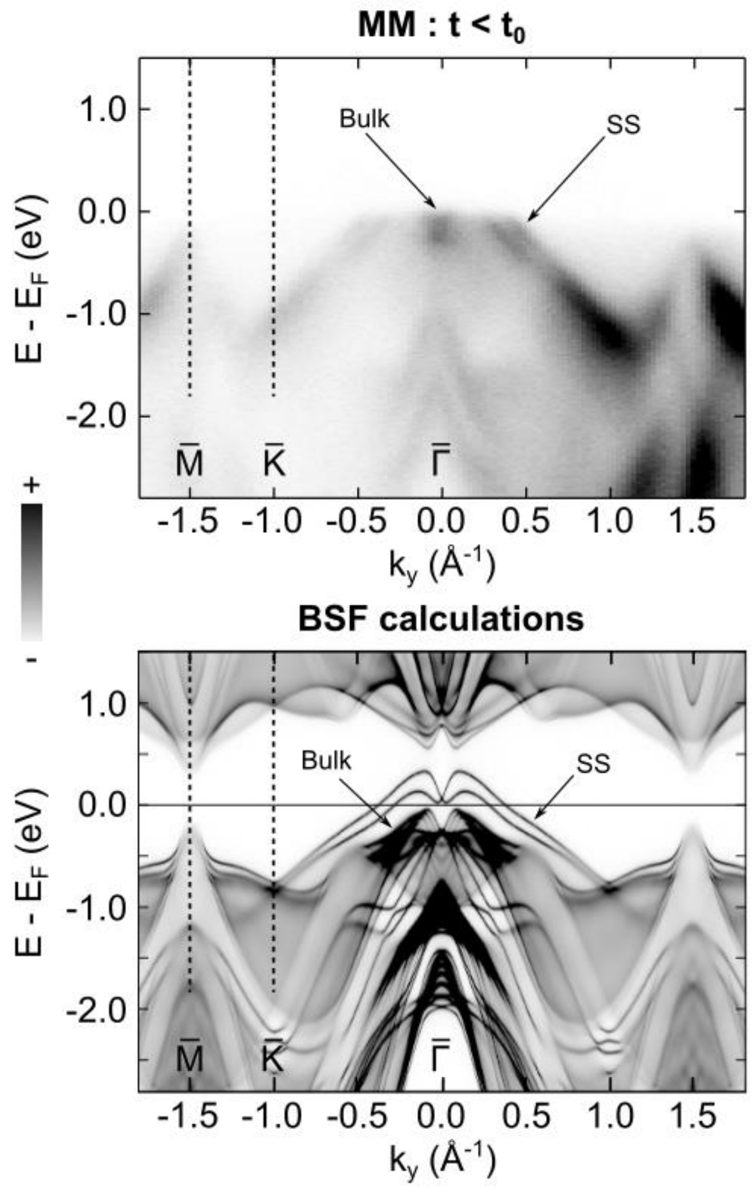
GeTe is a semiconductor with a band gap of about 0.8 eV.

Our thin films are p-doped and a downward band bending is expected:



Upon photoexcitation, a shift of the whole spectrum to higher binding energy is expected!

Transient ferroelectricity increase: origin



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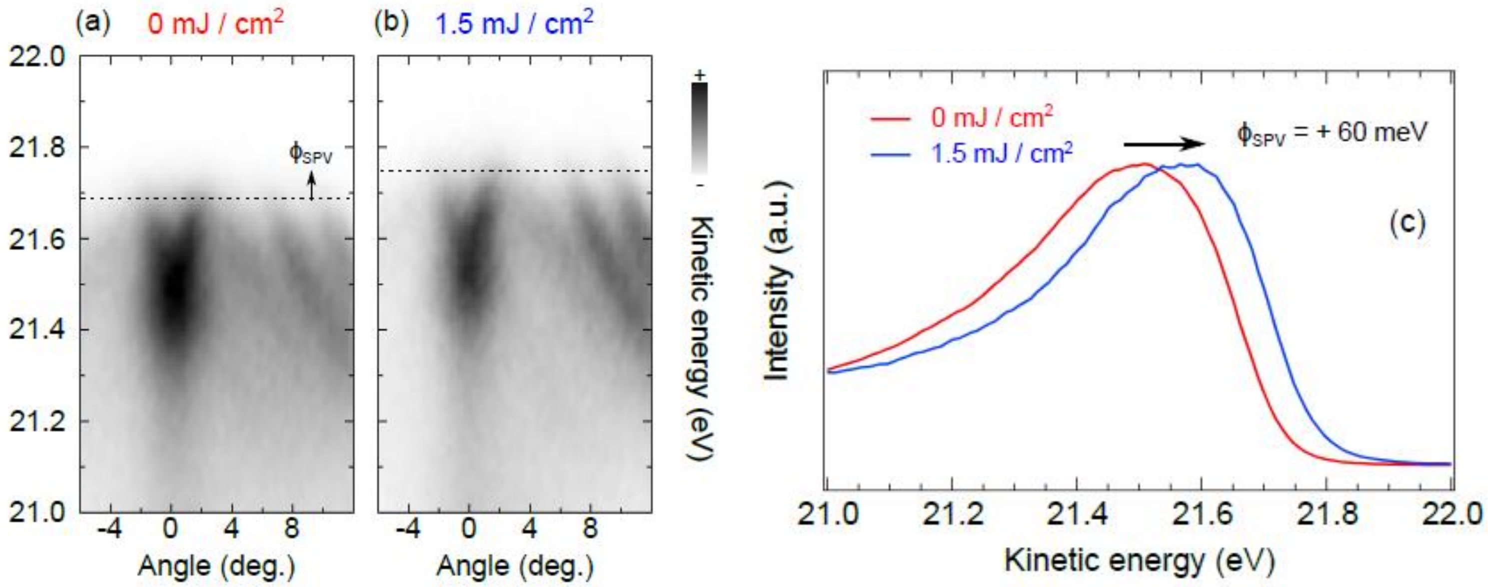

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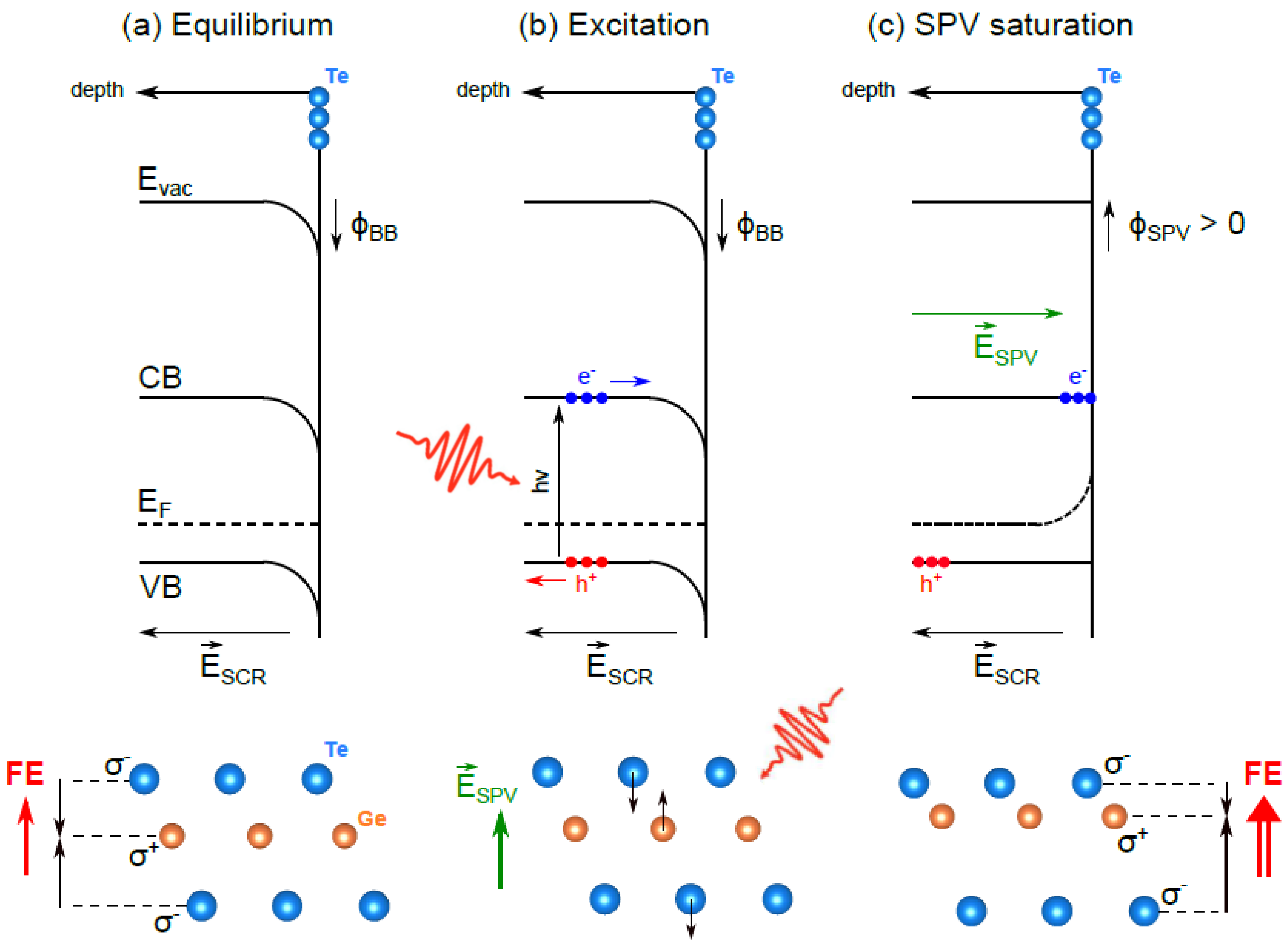
Transient ferroelectricity increase: origin

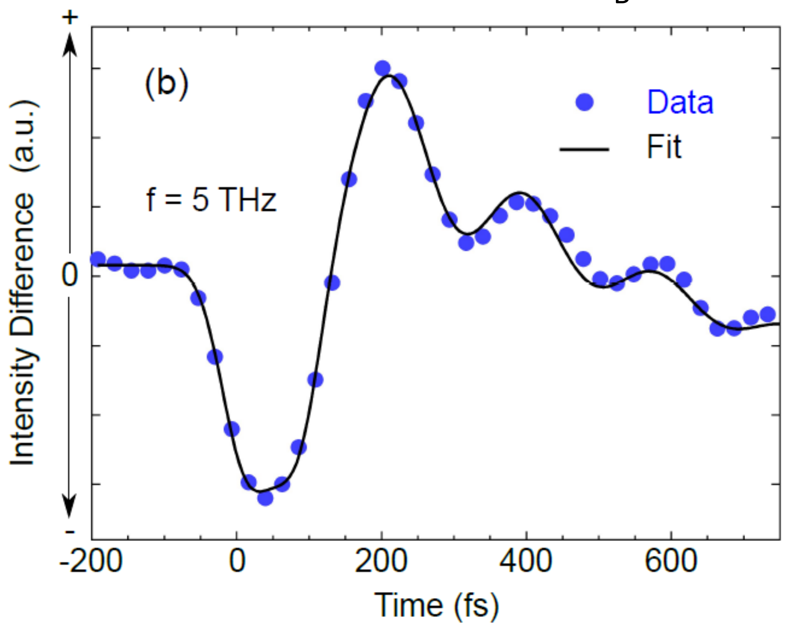


The surface photovoltage (SPV) generates a new electric field E_{SPV} at the surface

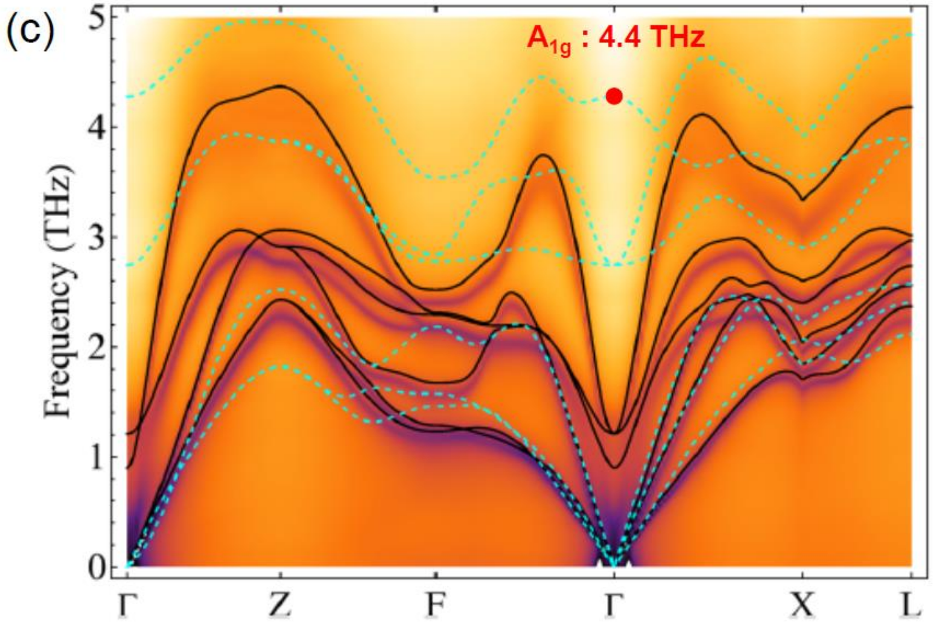
➢ This increases the ferroelectric distortion at the surface!

Coherent phonon mode at 5 THz?

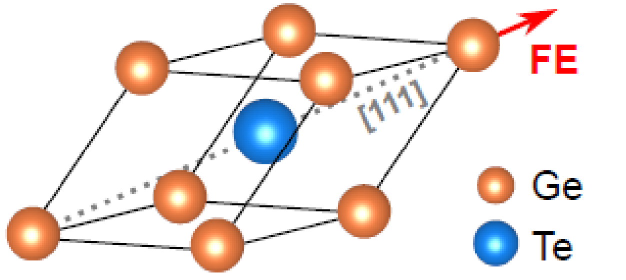
Transient intensity of CP_B point



Dashed blue lines: phonon dispersions in FE phase

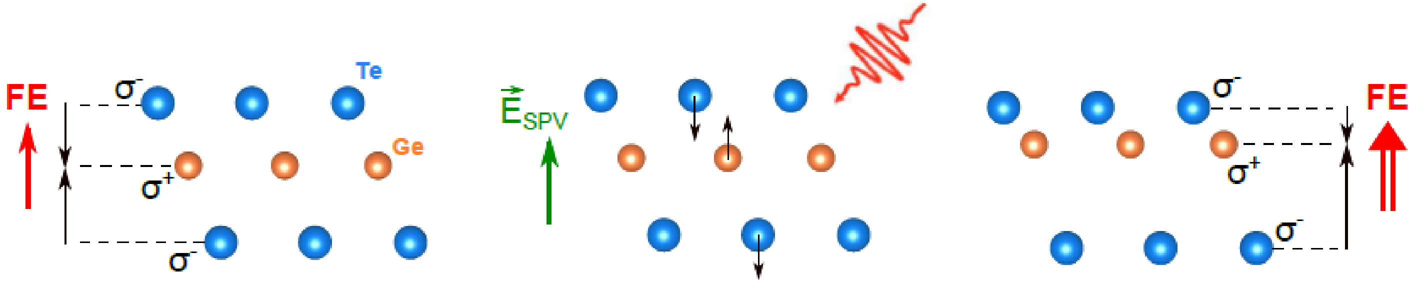


D. Dangic *et al.*, npj Computational Materials 2020



Ferroelectric mode along [111] direction

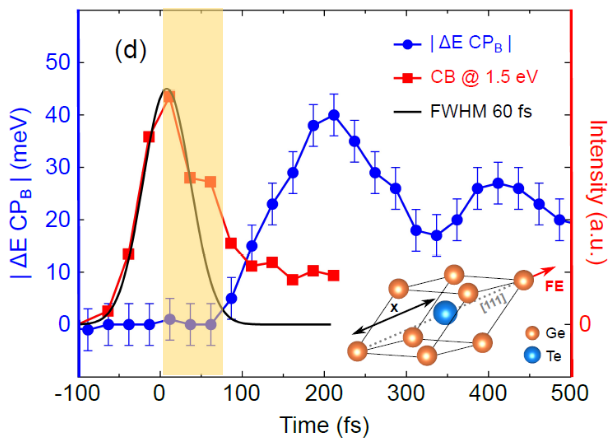
The frequency of the FE-related distortion oscillation is 15% larger than expected for the FE-mode at Γ.

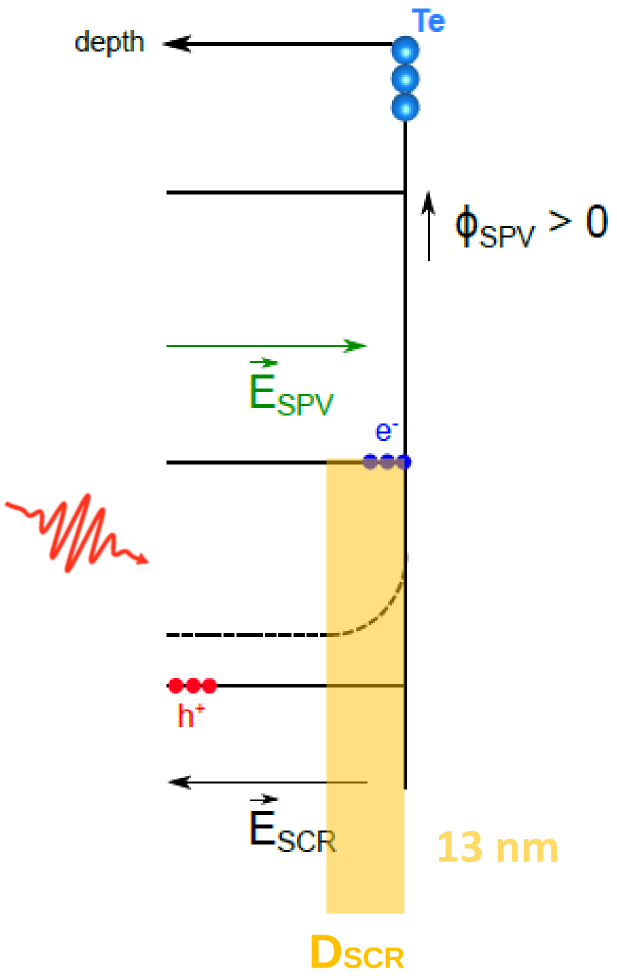


- The top layers get closer to each other: we propose that these **surface layers are stiffer** and the **phonon frequency are harder**!

Delayed ferroelectric increase

~ 80 fs





Build-up of surface photovoltage depends on the separation of holes and electrons in the space charge region (SCR) due to band bending.

Electron mobility:

$\mu_c = 100 \cdot 10^4$ m⁴/Vs

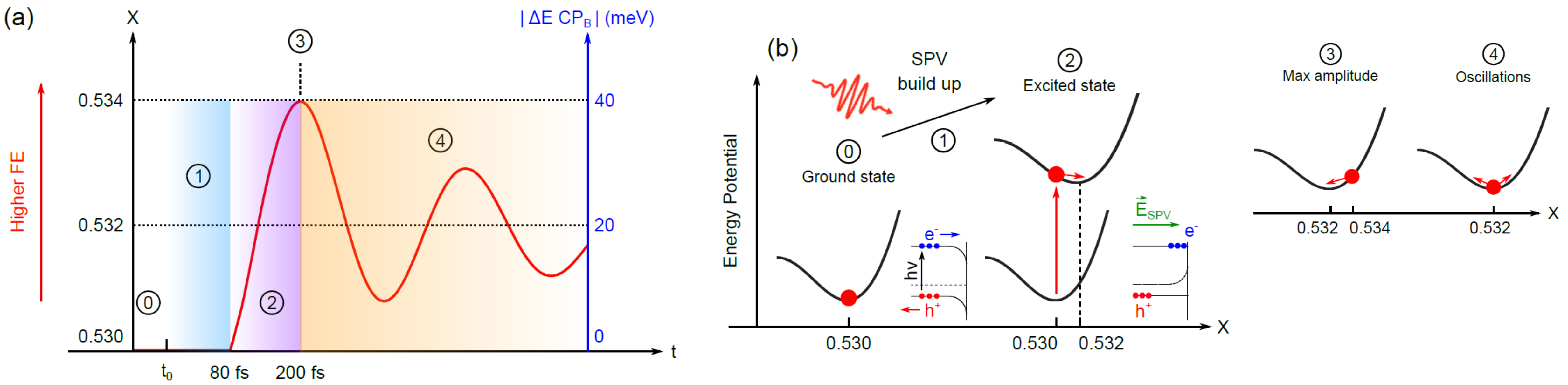
Electric field (SPV):

$E_{SPV} = 1 \cdot 10^7$ V/m

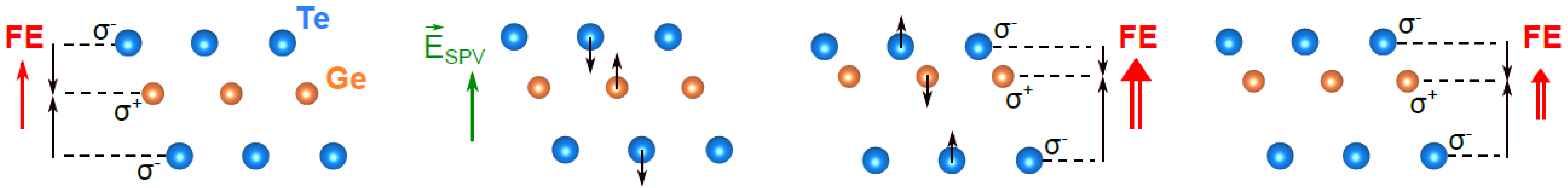
Estimated time for migration of electrons to surface: 100 fs

At t_0: photoexcitation of electrons/holes $\Longrightarrow$ electrons moves to surface and build-up SPV < 100 fs

Transient Enhancement of the Ferroelectricity in the Rashba Semiconductor α-GeTe



➢ Delayed displacive coherent phonon excitation



The enhancement of the ferroelectricity is a surface effect in thin film of GeTe

Thank you for your attention!