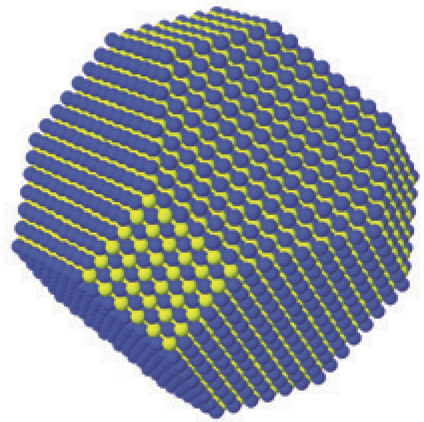
ON THE NATURE OF STRUCTURAL PHASE TRANSITION IN GeTe



THE PARENT COMPOUND OF PHASE-CHANGE MATERIALS

U. D. Wdowik(1), K. Parlinski(2), S. Rols(3), T. Chatterji(3), C. N. M. Kumar(4)

(1) Institute of Technology, Pedagogical University., Kraków, Poland
(2) Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland
(3) Institute Laue-Langevin, Grenoble, France
(4) Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, USA

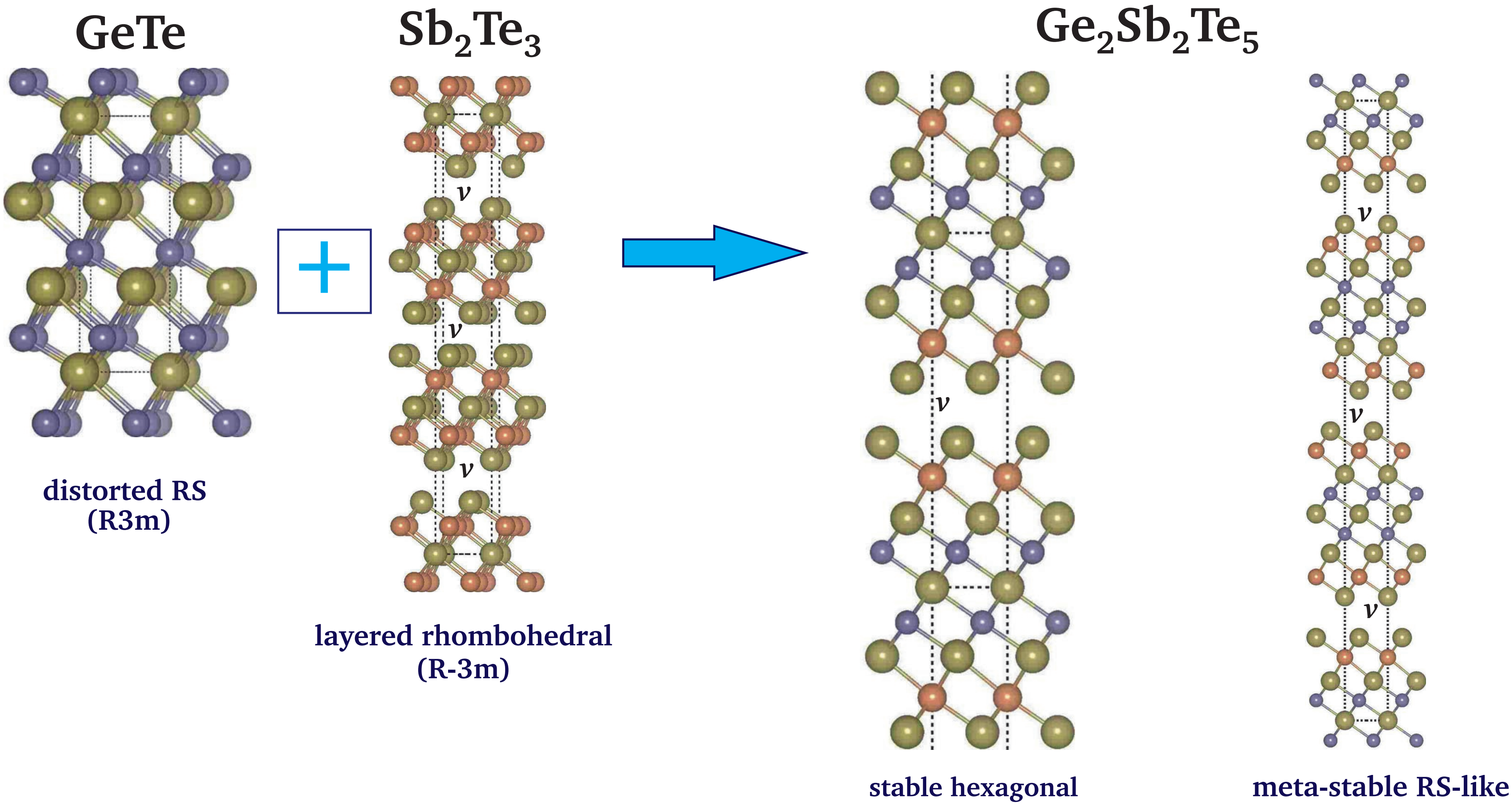
4th Workshop on ab initio phonon calculations, Kraków, Poland, 3-6 Dec., 2014

Phase-Change Materials

superlattices GST

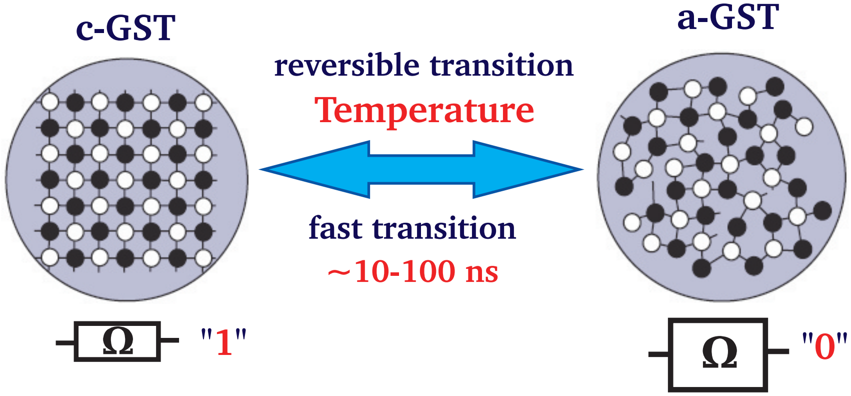
$$(GeTe)_m(Sb_2Te_3)_n = [(GeTe)_m(Sb_2Te_3)] + [(n-1)Sb_2Te_3]$$

Experiments
HRTEM, XRD, EXAFS



GST & their applications

Properties

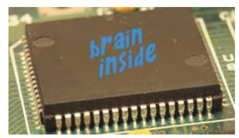


DIFFERENT
OPTICAL PROPERIES & RESITIVITIES
⇩
2-STATE SYSTEM
⇩
STORING 0 & 1 BITS

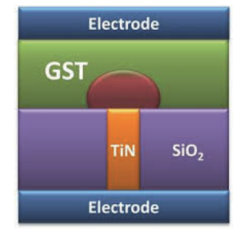
Applications

Optical storage devices
rewritable compact disks (CD-RW)
digital versatile disks (DVDs)
blu-ray disks (BDs)

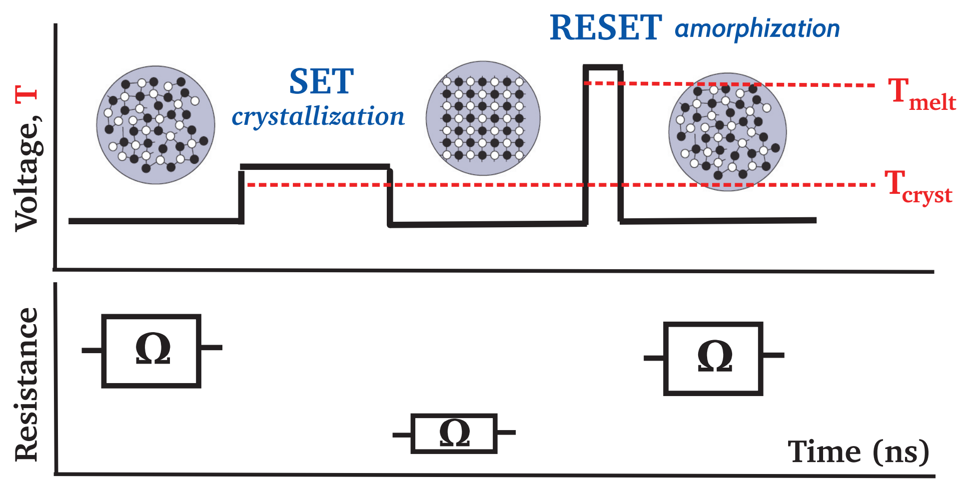
Reflectivity change
CD/DVD $Ge_2Sb_2Te_5 = (GeTe)_2 + Sb_2Te_3$
BD $Ge_8Sb_2Te_{11} = (GeTe)_8 + Sb_2Te_3$



Non-volatile memory devices
PCM-RAM
(phase change memory RAM)



Resistivity change (3-4 orders of magnitude)
PCMs $Ge_2Sb_2Te_5 = (GeTe)_2 + Sb_2Te_3$

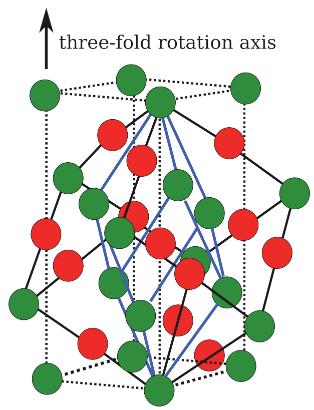


a- to c-phase transition induced by laser beam heating

GeTe

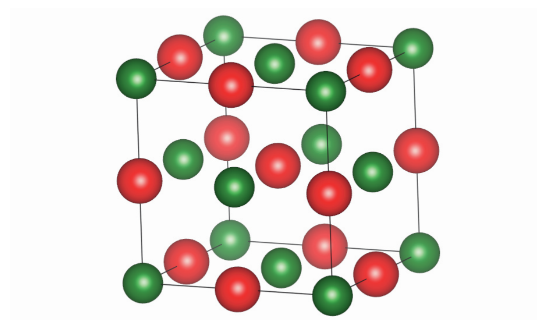
narrow-gap p-type semiconductor (0.1 - 0.2 eV)
+
hole concentration p ~ $(10^{20} \div 10^{21})/cm^3$

RHOMBOHEDRAL R3m



LT ferroelectric
Peierls distorted

ROCKSALT Fm-3m



HT paraelectric
distortions removed

T_c = 650(100) K

Ge-rich GeTe 733 K
Te-rich GeTe 633 K

3 short Ge-Te bonds 2.80 Å
3 long Ge-Te bonds 3.13 Å

polarization || trigonal axis
~60 μC/cm²

E_{CAL} = 0.48 eV

single Ge-Te bond ~3.0 Å

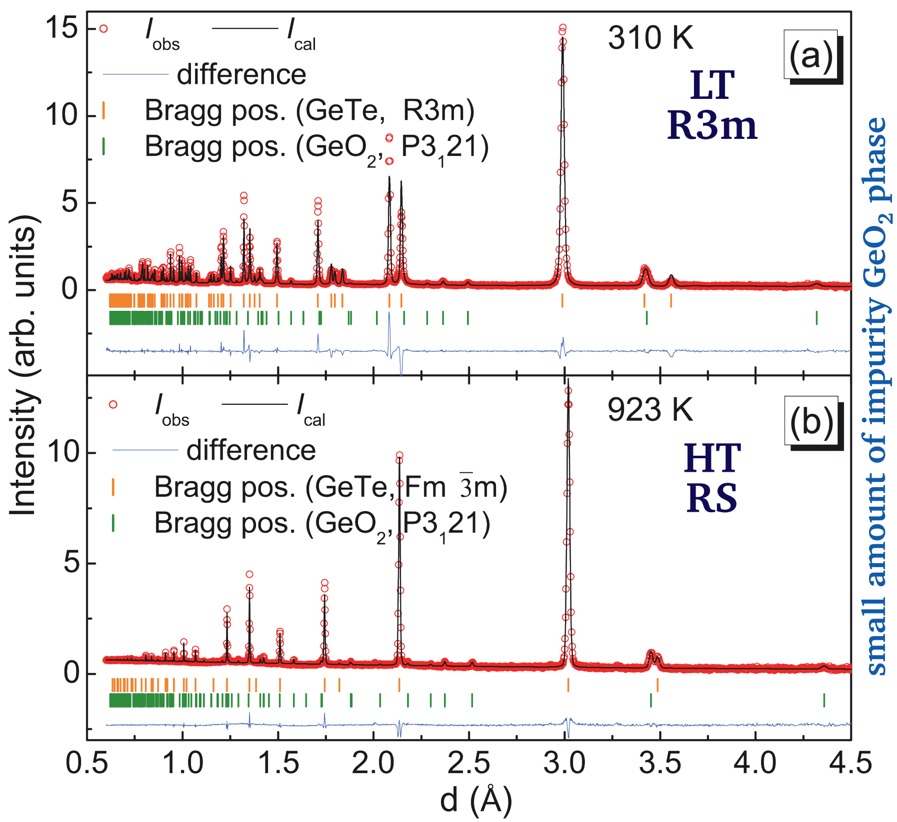
E_{CAL} = 0.26 eV

PHASE TRANSITION IN GETE - EXPERIMENTS

SAMPLE

Alfa Aesar powder sample
claimed to be 99.999% pure
Mesh = 200

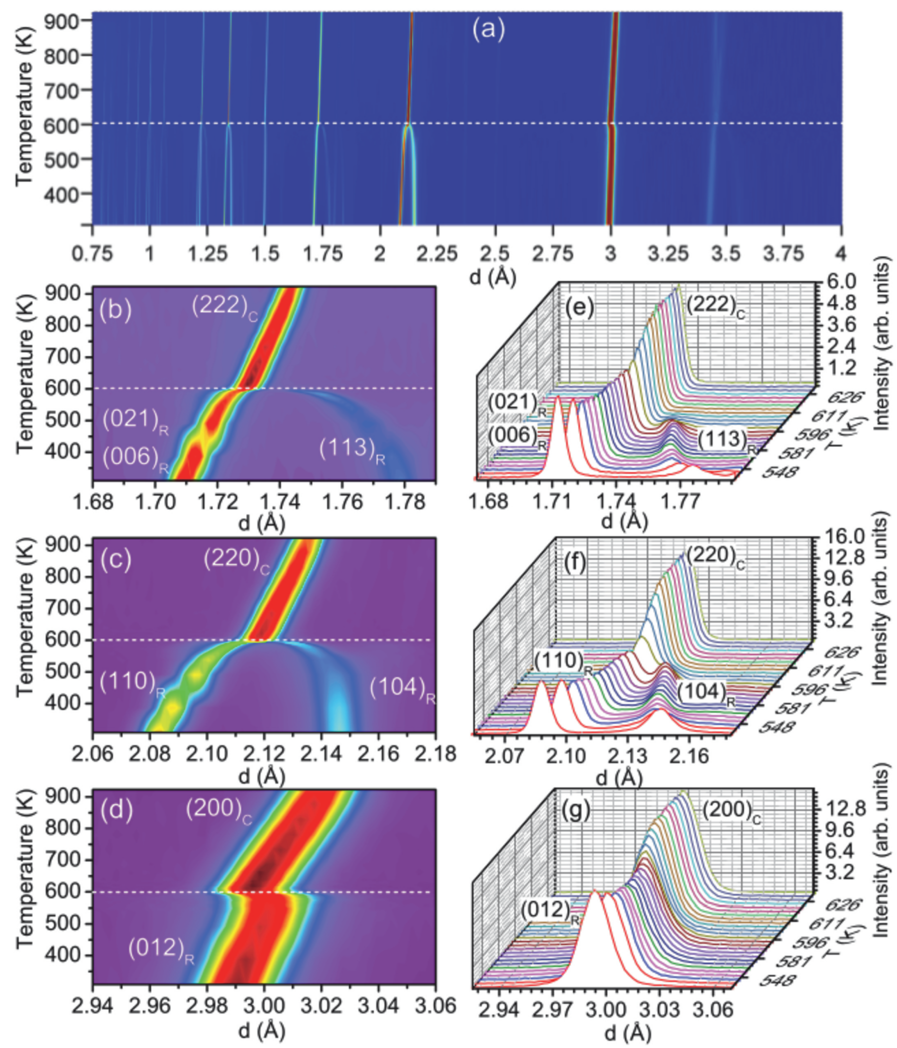
XRD patterns for LT and HT phases of GeTe



Rietveld profile refinement by FULLPROF
[J. Rodriguez-Carvajal, http://www.ill.eu/sites/fullprof]

NEUTRON POWDER DIFFRACTION

TOF powder diffractometer POWGEN
Spallation Neutron Source @ Oak Ridge National Lab. USA
neutron central wavelength 1.333 Å
d-spacing 0.42 - 5.4 Å

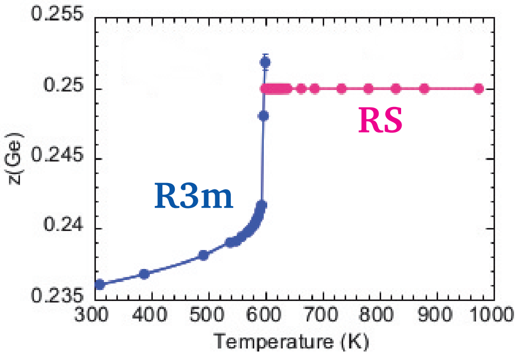


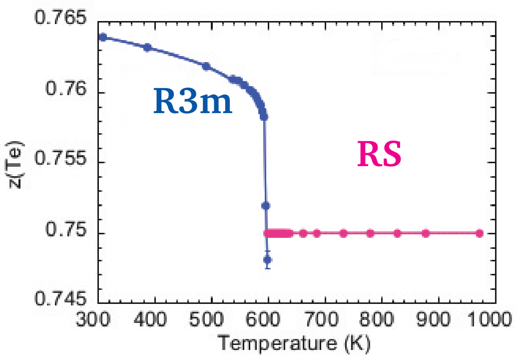
PHASE TRANSITION IN GETE - EXPERIMENTS

Vanishing distortions $T > T_c$

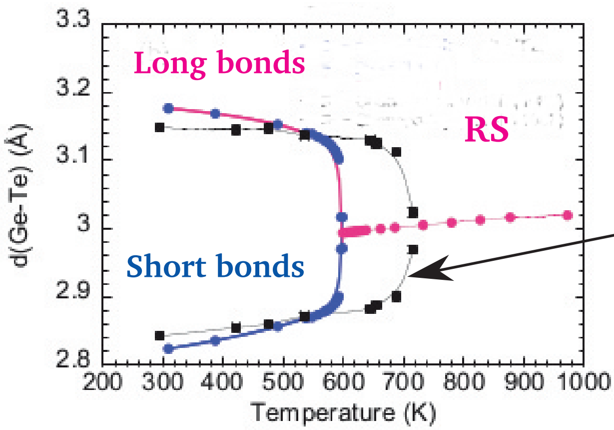
$T_c = 600$ K

positional parameters in hex. representation





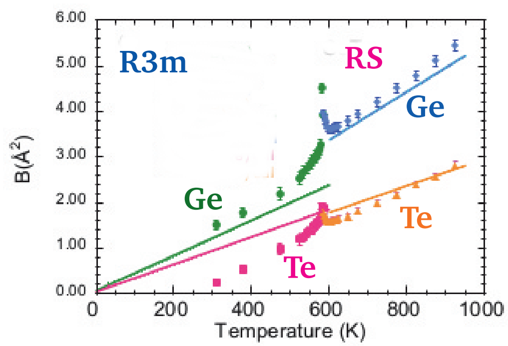
$\Delta z(Ge)=0.25-z = \Delta z(Te)=z-0.75$



GeTe single crystal

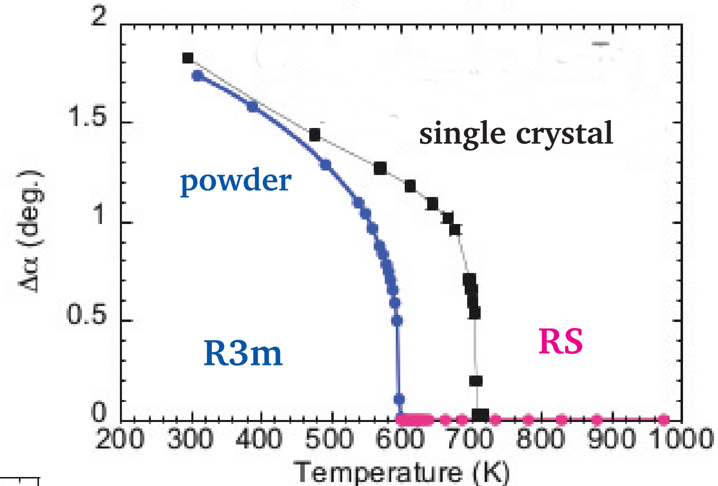
Chattopadhyay et al.

J. Phys. C 20, 1431 (1987)



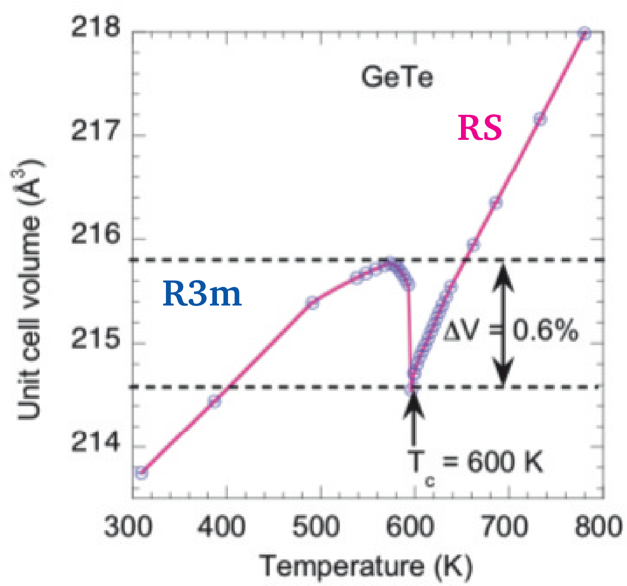
distortion angle

$\Delta\alpha=90°-\alpha$



pseudo-cubic setting

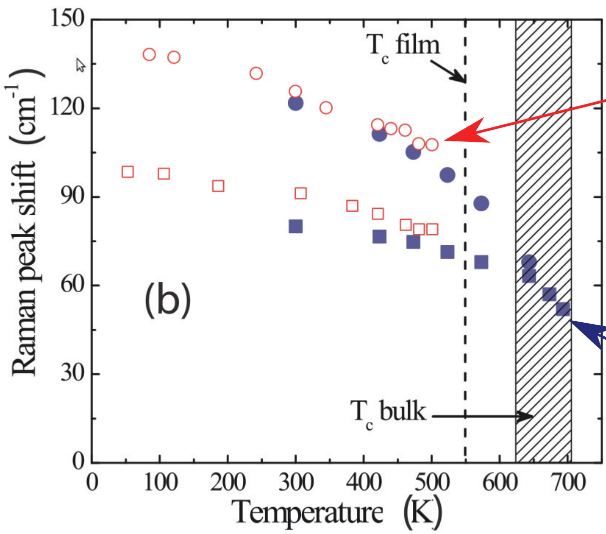
Volume reduction @ T_c ~ 1%



Long-standing question: displacive or order-disorder ?

Displacive

Raman scattering

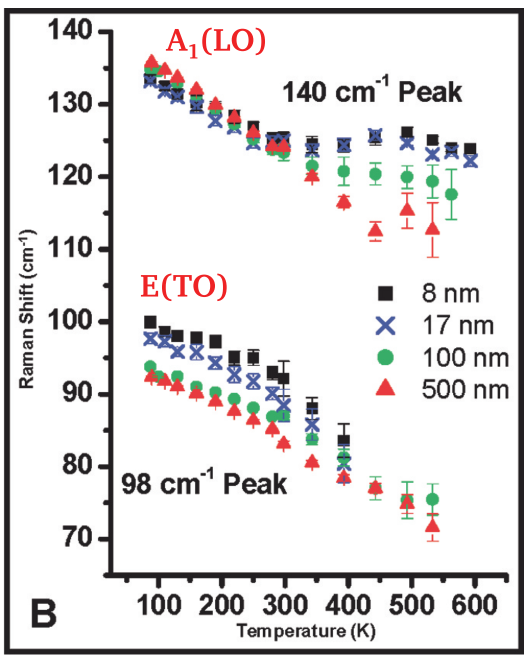


single crystal

Solid State Comm. 8, 1275 (1970)

sputtered thin films

PRB 82, 115209 (2010)



GeTe nanocrystals

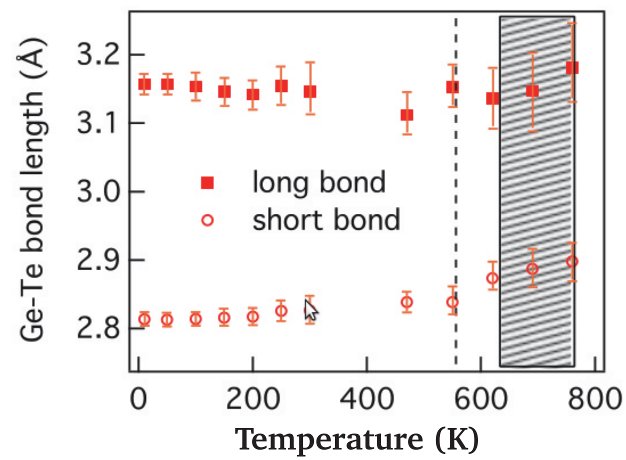
NanoLett 11, 1147 (2011)

A_1(LO) & E(TO)
vanish @ T_c

Persisting distortion $T > T_c$

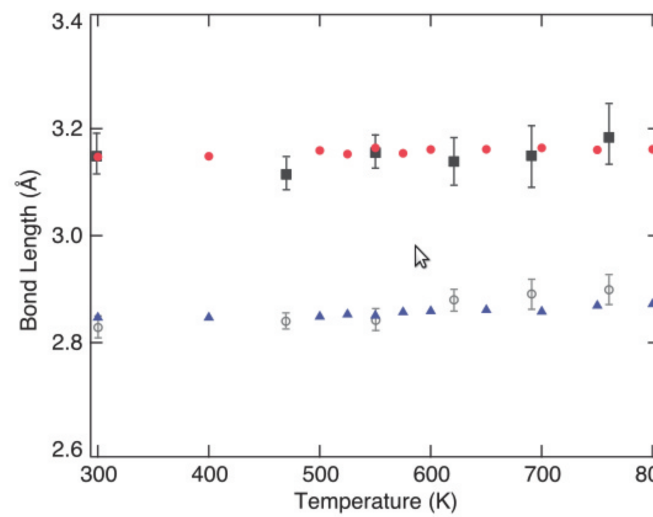
Order-disorder

EXAFS on films



PRB 82, 155209 (2010)

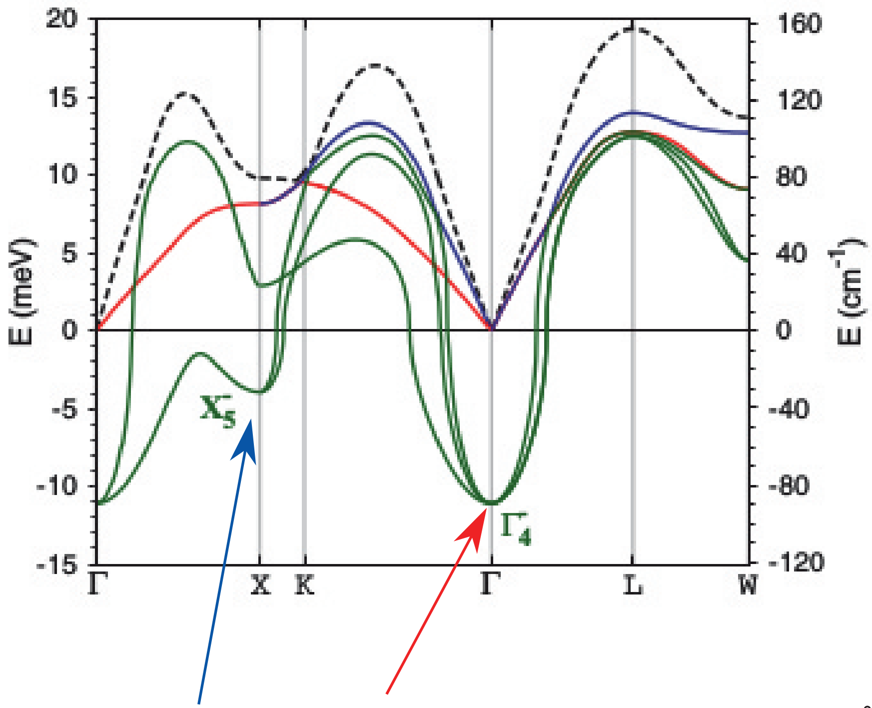
PDF analysis on films



Appl. Phys. Lett. 99, 231907 (2011)

EXASF & PDF performed by the same experimental group

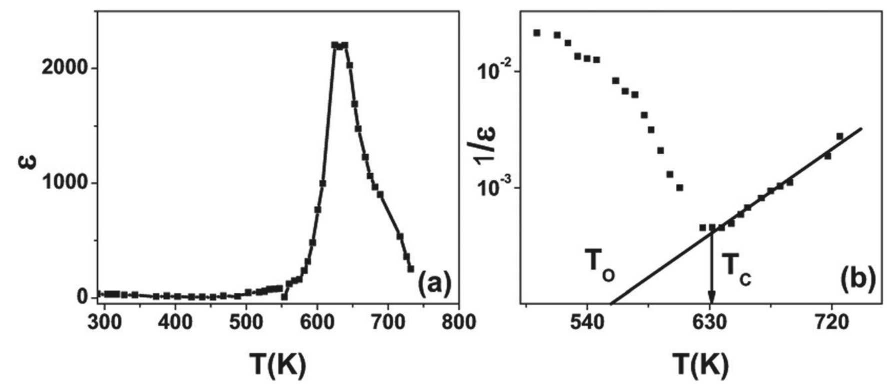
GeTe - RS



3.93i meV

11.10i meV
triply degenerate
T_{1u} (TO)

a_{EXP} = 6.01-6.02 Å
a_{CAL} = 6.011 Å



J. App. Phys. 112, 052018 (2012)

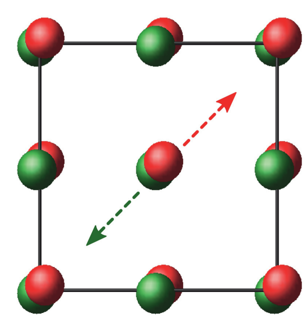
Calculated ϵ^{∞} ~ 100
Experimental ϵ^{∞} ~ 2000 (just above T_c)
Calculated Born Z* ~ 10
Calculated E_{GAP} 0.24 eV

GM4- with 3 components condensed

Group theory

3-dim GM4- Irrep (order parameter consists of 3 components)

Fm-3m ⟹(GM4-, $e_1 \neq 0$, $e_2 = e_3 = 0$)⟹I4mm
Fm-3m ⟹(GM4-, $e_1 = e_2 \neq 0$, $e_3 = 0$)⟹Imm2
Fm-3m ⟹(GM4-, $e_1 = e_2 = e_3 \neq 0$)⟹R3m

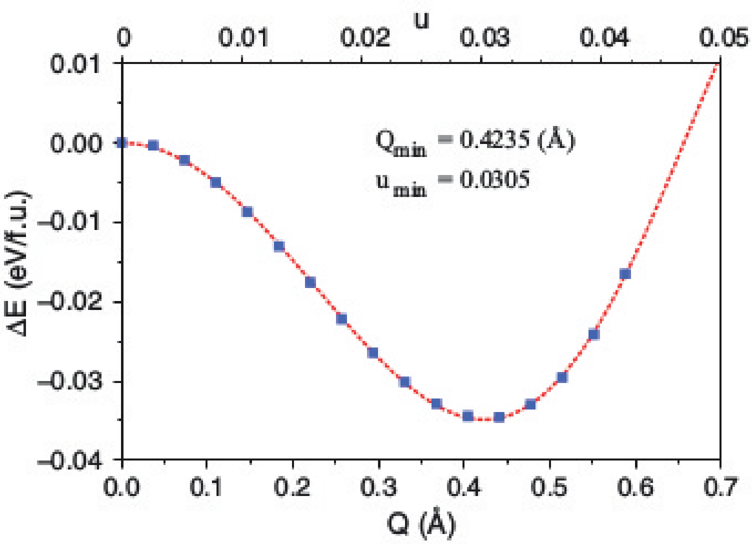


relatice displacements of Ge and Te sublattices along cubic cell diagonal ([111] dir)

Condensation of 3 components lowers Fm-3m to R3m

GeTe - R3m

Relative energy vs. amplitude Q of the unstable GM4-



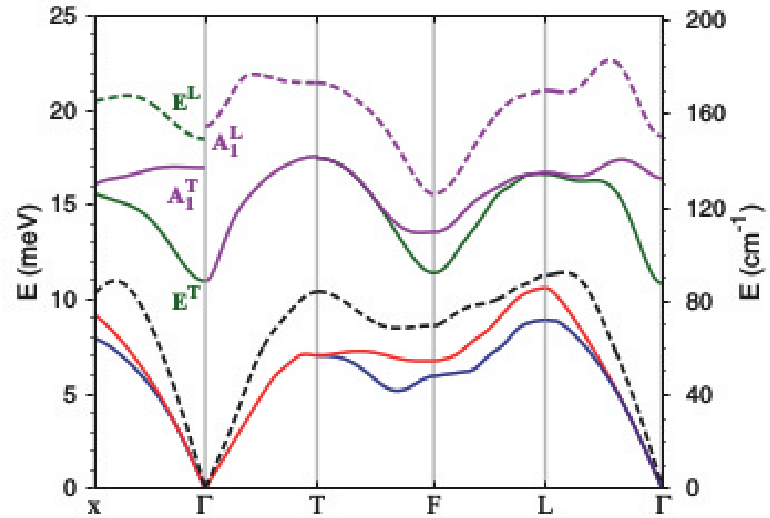
$$\Delta E = 1/2a\,Q^2 + 1/4b\,Q^4 + 1/6c\,Q^6$$
$$a < 0,\ b > 0,\ c < 0$$

Q_{min} = 0.424 Å , u_{min} = 0.03 (0.316 Å)
E_{GAP} = 0.48 eV

	pseudo-cubic cal.	pseudo-cubic exp.		rhombohedral cal.	rhombohedral exp.
a_c	6.085	5.982	a_r	4.373	4.294
α_c	88.110	88.247	α_r	57.864	58.032
u	0.030	0.027	x	0.234	0.236

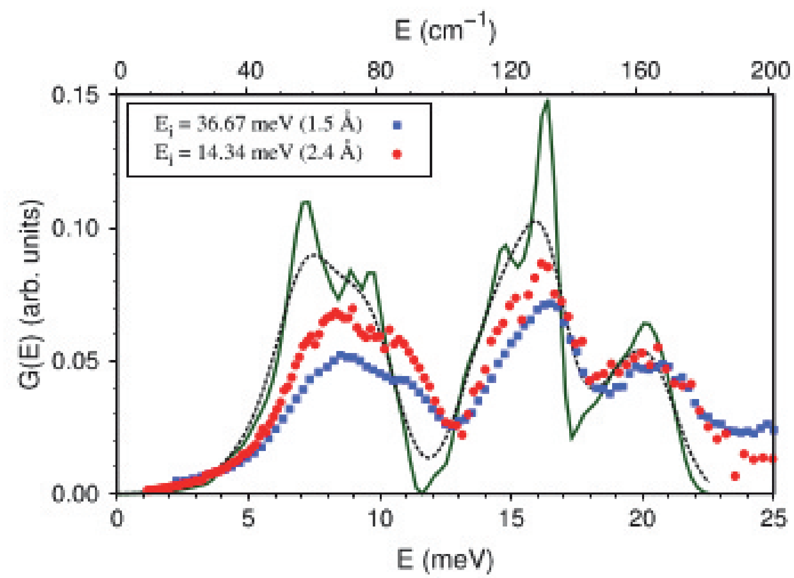
Exp. (309 K) neutron diffraction (spallation source)

Phonons in R3m - configuration (Q_{min}, E_{min})



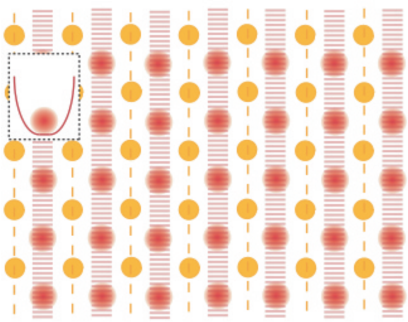
	⊥	∥	<>	Exp. (reflectivity)
ϵ∞	**39.21**	**34.56**	**37.66**	**35-37.5**
Z*	**5.42**	**3.30**	**---**	

IN4C (TOF spectrometer), ILL



PRB 89, 224306 (2014)

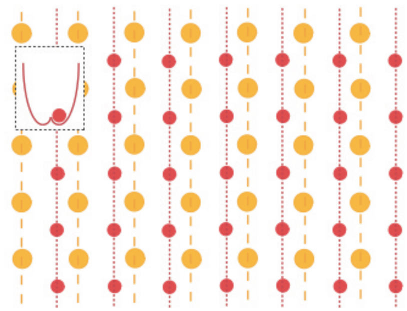
Phase transition in GeTe



single local potential minimum

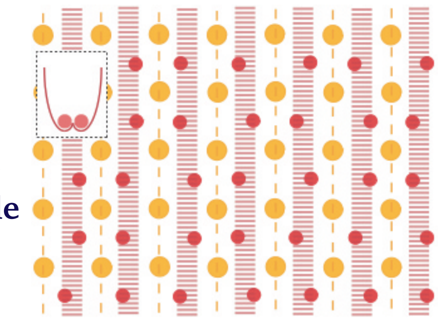
DISPLACIVE ←

involves soft mode



ORDER-DISORDER →

may involve soft mode



several local potential minima

How to resolve whether the local atomic potential is single or multiwell

local atomic potential barrier described by on-site $F_{ii}(\mu)$

Schneider & Stoll
PRB 13, 1216 (1976)

$F_{ii}(\mu) > 0$ → **SINGLE MINIMUM**

$F_{ii}(\mu) < 0$ → **MULTIWELL**

F_{ii}(Ge,Te) in GeTe-RS

$F_{xx}(Ge) = F_{yy}(Ge) = F_{zz}(Ge) = +30.141$ N/m

$F_{xx}(Te) = F_{yy}(Te) = F_{zz}(Te) = +53.974$ N/m

single minima of local potentials
for Ge & Te atoms in GeTe-RS

DISPLACIVE PHASE TRANSITION IN GeTe

paraelectric-to-ferroelectric phase transition in **LiNbO3**

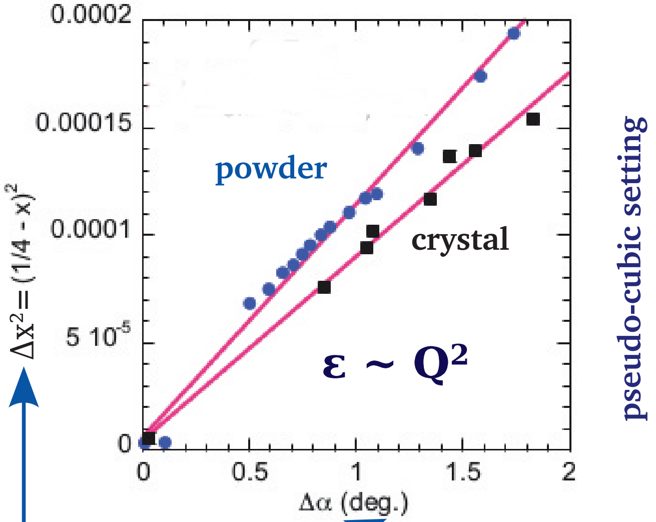
$F_{zz}(Li) < 0$, remaining $F_{ii}(Li)$, $F_{ii}(Nb)$, $F_{ii}(O) > 0$

double minimum curve
for local potential of Li along z

ORDER-DISORDER PHASE TRANSITION IN $LiNbO_3$

PRB 61, 272 (2000)

1ST OR 2ND ORDER PHASE TRANSITION ?



strain ε - secondary OP
breaks symmetry elements

Q - primary OP
driving force of ferroelectricity
in GeTe below T_c

Landau expansion **F(Q,ε)**

⇩

$\varepsilon \sim Q^2$

⇩

2nd order phase transition

Conclusions

Structural phase transition in GeTe is driven by the condensation of exactly 3 components of the triply degenerate optical transverse soft-phonon mode at the Brillouin zone center.

Phase change in crystalline GeTe is displacive in its origin.

Structural phase transition in GeTe is of 2^{nd} order.

Thank you for your attention