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**Simulations of phase change materials: Order-disorder phase transitions in
nanoseconds**

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Simulations of phase change materials: Order-disorder phase transitions in nanoseconds

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“Modern” personal computer: Long wait after switching on. Why?



Random access memory (RAM) is “volatile” [contents vanish if no power]

Non-volatile memory? Yes, USB sticks (Si/SiO₂ arrays), DVD-RAM (Ge₂Sb₂Te₅ alloy)

Battle between Blu-ray Disc (BD) and HD-DVD decided 2008:

HD-DVD kontra blu-ray: Warner wird blu-ray exklusiv, Formatkrieg entschieden?



Wal-Mart adopts Blu-ray, dumps HD DVD format

Due to customer demand, Wal-Mart will exclusively be offering Blu-ray hardware and DVDs by the middle of this year

By Agam Shah, IDG News Service
February 15, 2008

Wal-Mart, the largest U.S. retailer, on Friday said it would phase out the sales of HD DVD offerings and exclusively offer high-definition Blu-ray hardware and DVDs by the middle of this year

Toshiba drops HD DVD; Blu-ray wins

by Ross Miller Feb 16th 2008 1:15PM
Filed under: Culture, Sony PlayStation 3, Microsoft Xbox 360, Business

The rumors were true. Japanese news source NHK (english translation and Reuters validation) is reporting that Toshiba is planning to drop support of HD DVD, striking a final blow to the format and conceding victory to Blu-ray. The Sony-backed high-definition disc has been gaining strides for some time, most notably after Warner Bros switched to Blu-ray exclusively. Toshiba is expected to face hundreds of millions of dollars in losses.

“Phase change (PC) memories”

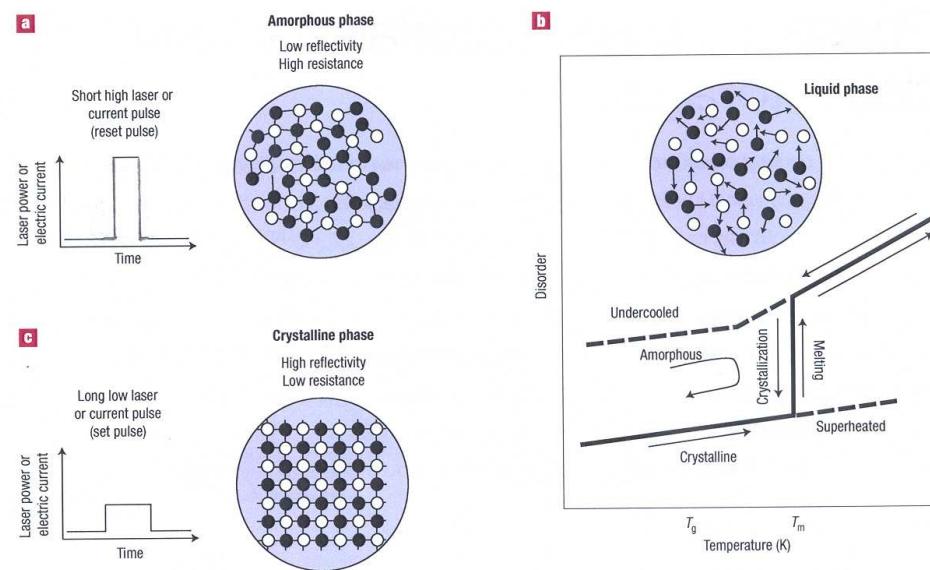
Phase change memories

S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968)

“Reversible electrical switching phenomena in disordered structures”

Rapid and **reversible** transition between resistive and conducting state in semiconductor films (caused by electric field).

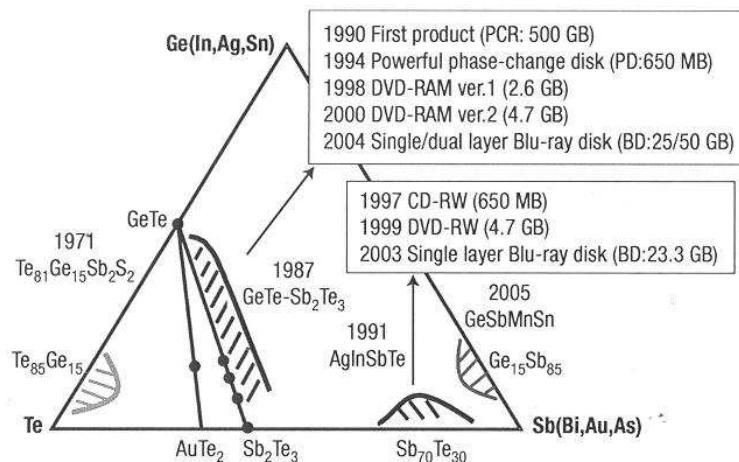
Current view: Transition between crystalline (conducting) and amorphous (resistive) states.
Can use laser pulses to cause reversible transitions in nanosized “bits” in a film



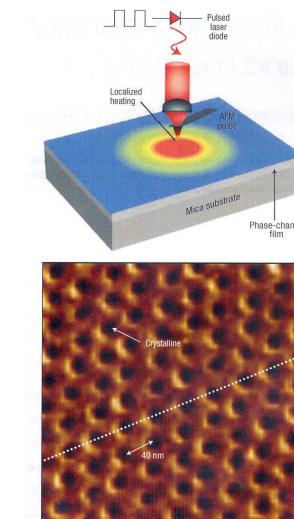
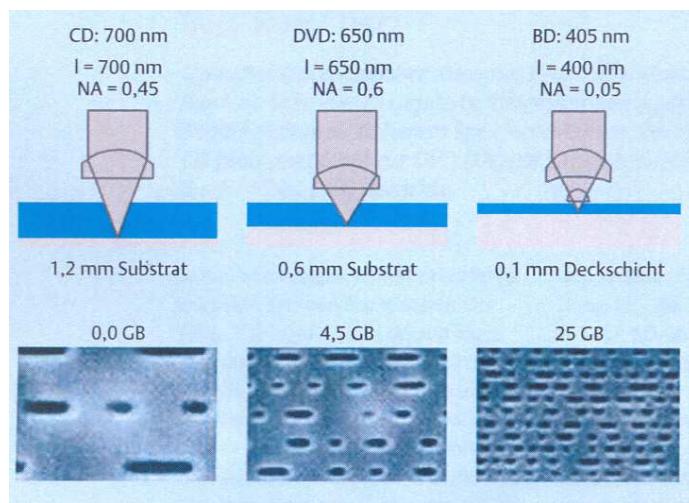
“Melt-quench” stage (~ 1 ns), “crystallization” stage ($20 - 100$ ns)

Which semiconductors? Many Ge/Sb/Te alloys

GeTe: M. Chen, K. A. Rubin, R. W. Barton, Appl. Phys. Lett. **49**, 502 (1986).

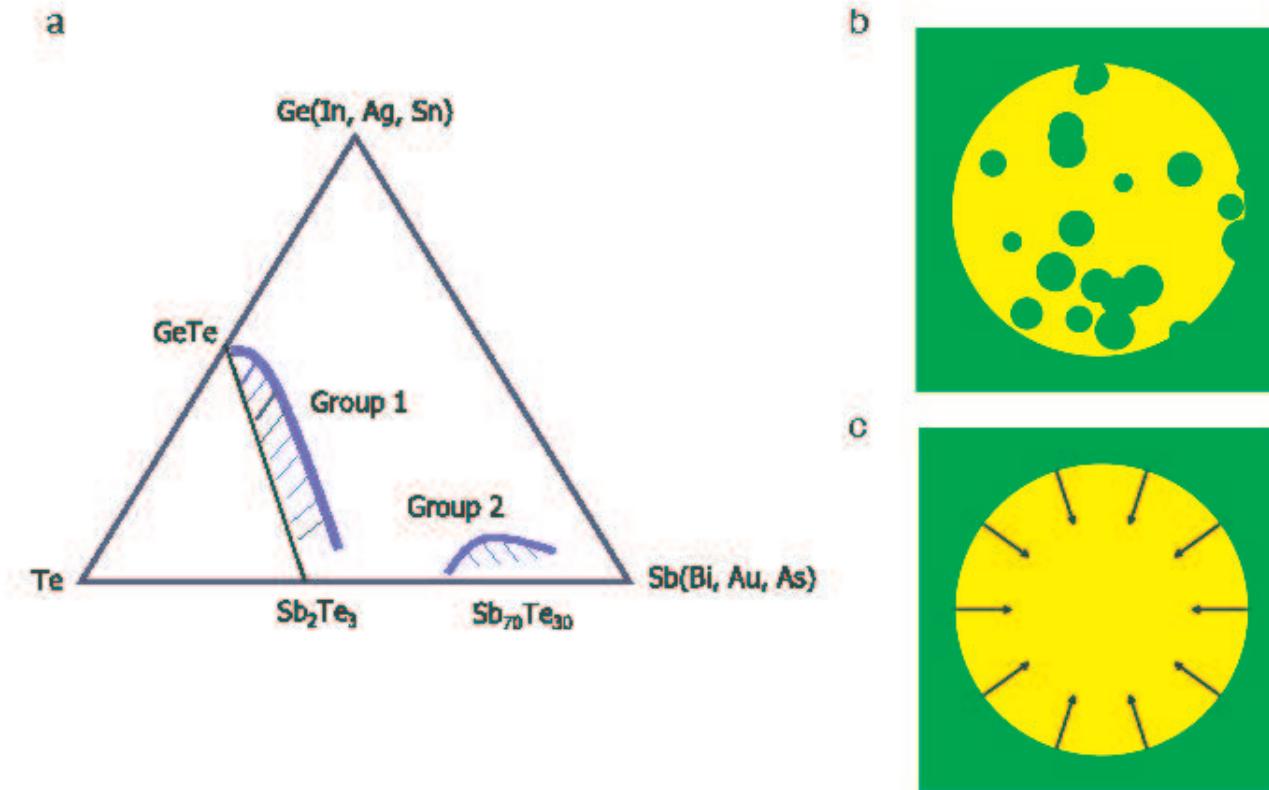


Technical progress:



H. F. Hamann et al. (IBM, 2006) 500 GB cm⁻² !!

Two main families with different crystallization mechanisms:
Ge/Sb/Te (GST) and doped Sb/Te (near eutectic) alloys



GST: nucleation from inside bit

AIST: growth from crystalline surroundings

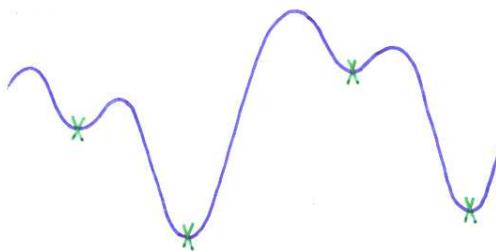
Simulation of structural phase transitions:

Geometric structure: is a central problem in condensed matter physics, chemistry, biology

“If you want to study **function**, study **structure**”

Francis Crick, *What mad pursuit*, (Penguin, 1988), p. 150.

Need a method to calculate energy surfaces $E(R_I)$: R_I : ionic positions



- without adjustable parameters (if possible) and for many atoms (100's to 1000's), time scales $O(1 \text{ ns})$

Density functional calculations of ground state properties (here $E(R_I)$)

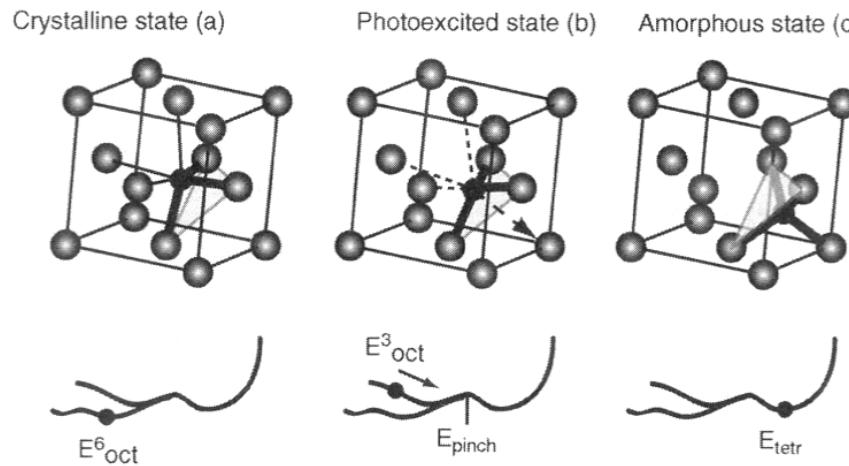
Combination of DF calculations with molecular dynamics (R. Car and M. Parrinello)

Follow trajectories of ions moving under forces calculated using DF method

Present limitations of DF calculations: few hundred atoms, some hundreds of picoseconds

Phase change materials ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ is prototype): Why is crystallization so rapid?

“Umbrella model”: **Kolobov et al.** (2004)



Model structure for $\text{Ge}_1\text{Sb}_2\text{Te}_4$: **Wełnic et al.** (2006)

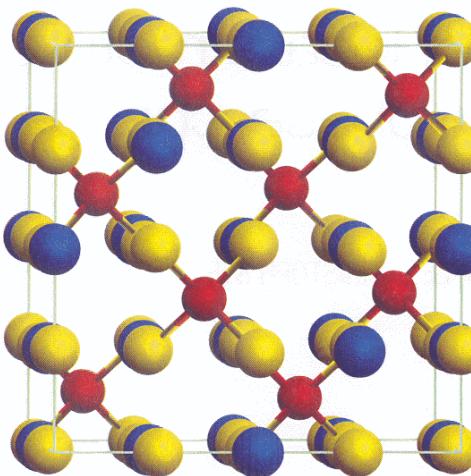
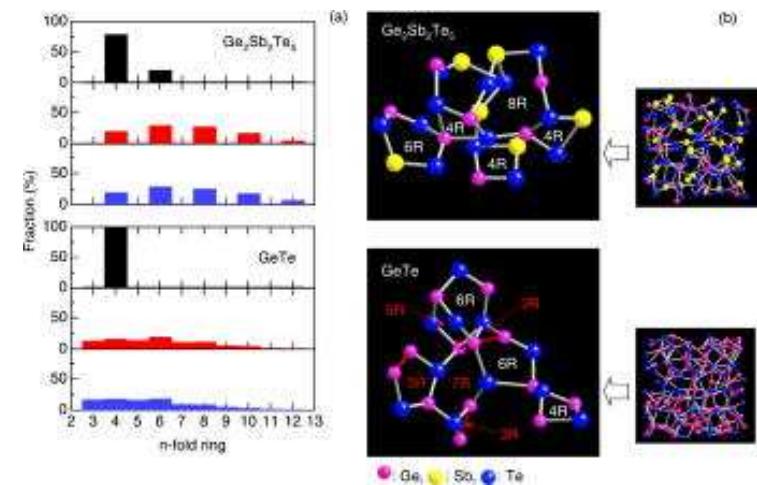
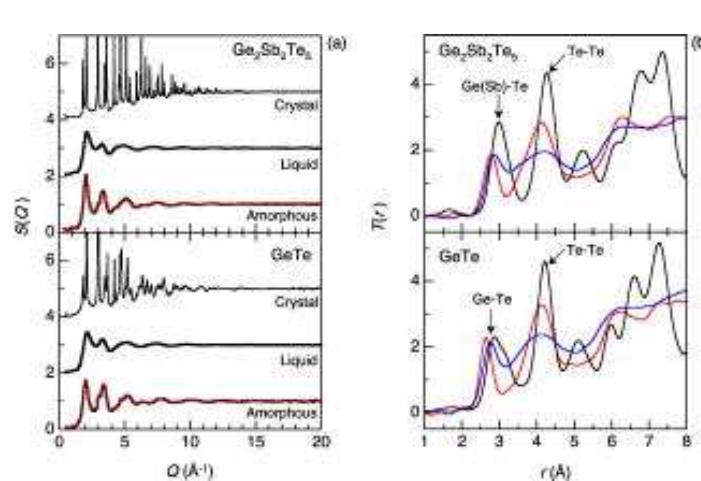


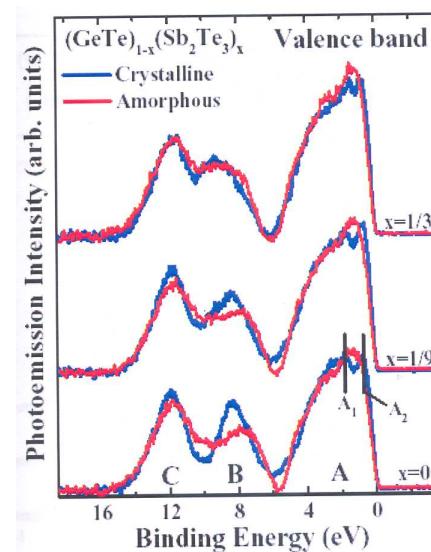
Figure 1 Structural model for $\text{Ge}_1\text{Sb}_2\text{Te}_4$ in the spinel phase (Ge = red, Sb = blue, Te = yellow) shown in a supercell containing 56 atoms. The plot shows that the spinel structure can be understood as a compromise between the purely octahedrally bonded rocksalt and the purely tetrahedrally bonded chalcopyrite phase.

$\text{Ge}_2\text{Sb}_2\text{Te}_5$: new experiments (SPring-8):

XRD: S. Kohara *et al.* Appl. Phys. Lett. **89**, 201910 (2006)



XPS: J.-J. Kim *et al.* Phys. Rev. B **76**, 115124 (2007)



JUBL. IBM Blue Gene/L (installed January 2006)

JUGENE. IBM Blue Gene/P (installed 2008, expanded May 2009)



MD/DF possible on PC materials (e.g. $\text{Ge}_2\text{Sb}_2\text{Te}_5$) with “large” samples over “long” times:

Ge₂Sb₂Te₅: (material of DVD-RAM)

J. Akola and R. O. Jones, Phys. Rev. B **76**, 235201 (2007)

- 10% vacancies
- liquid —> amorphous transition also metal —> semiconductor transition
- order-disorder transition (time scale?). Why is it so rapid?

Strategy:

- Simulation of 460 atoms (102 Ge, 102 Sb, 256 Te), 52 vacancies initially in NaCl structure (Na: Te, Cl: random Ge, Sb, vacancies)
- Melt (3000 K), cool to MP (900 K, 42 ps) data collection 21 ps
- Cool to 300 K (139 ps), data collection 21 ps
- Quench using simulated annealing to 100 K (74 ps)
- Car-Parrinello method, Pseudopotential: Troullier-Martins, E_{xc} : Perdew, Burke, Ernzerhoff (1996), plane wave basis cutoff 20 Ry.)

All components “heavy” elements, relatively compact PW basis,
Born-Oppenheimer dynamics with long time steps (use of predictor-corrector algorithm).

S. Caravati et al., Appl. Phys. Lett. **91**, 171906 (2007)

J. Hegedüs and S. R. Elliott, Nature Mater. **7**, 399 (2008)

RDF of a -GST and ℓ -GST at 300 K:

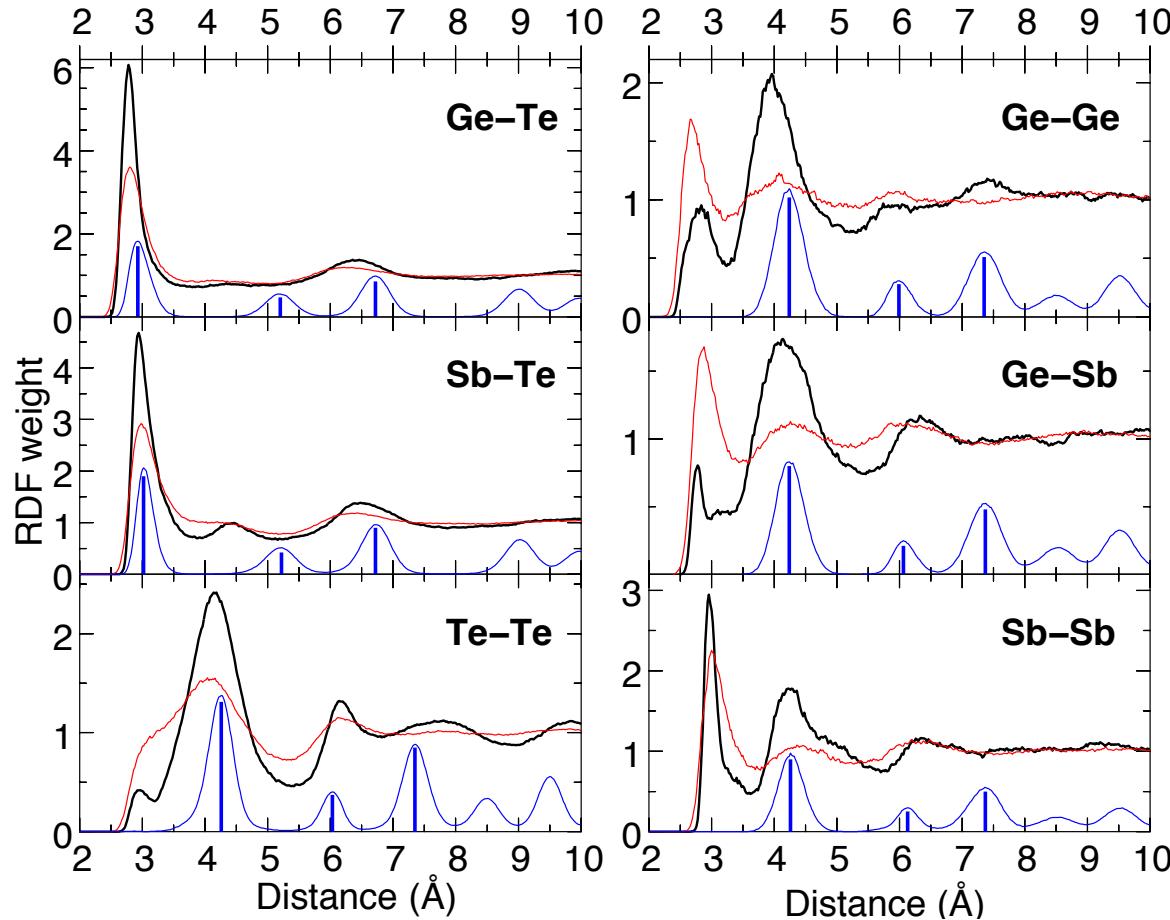


Figure 1: Partial RDF of a - (thick black) and ℓ -GST (red). Blue curve and bars are for c -GST at 300 K (with different scale).

GST coordination numbers: **Ge**: 4.2, **Sb**: 3.7, **Te**: 2.9 (cf. “8-N rule”: 4, 3, 2)

Medium- to long-range order of Te atoms in a “disordered” material !!!

Ring configurations in a-GST and a-GeTe at 300 K:

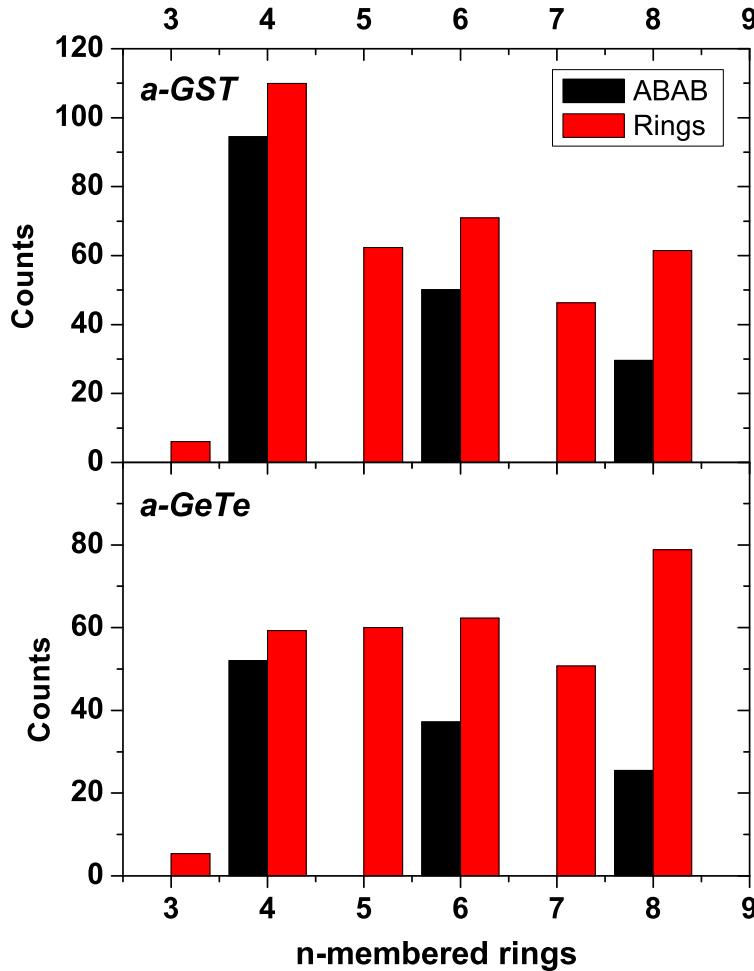
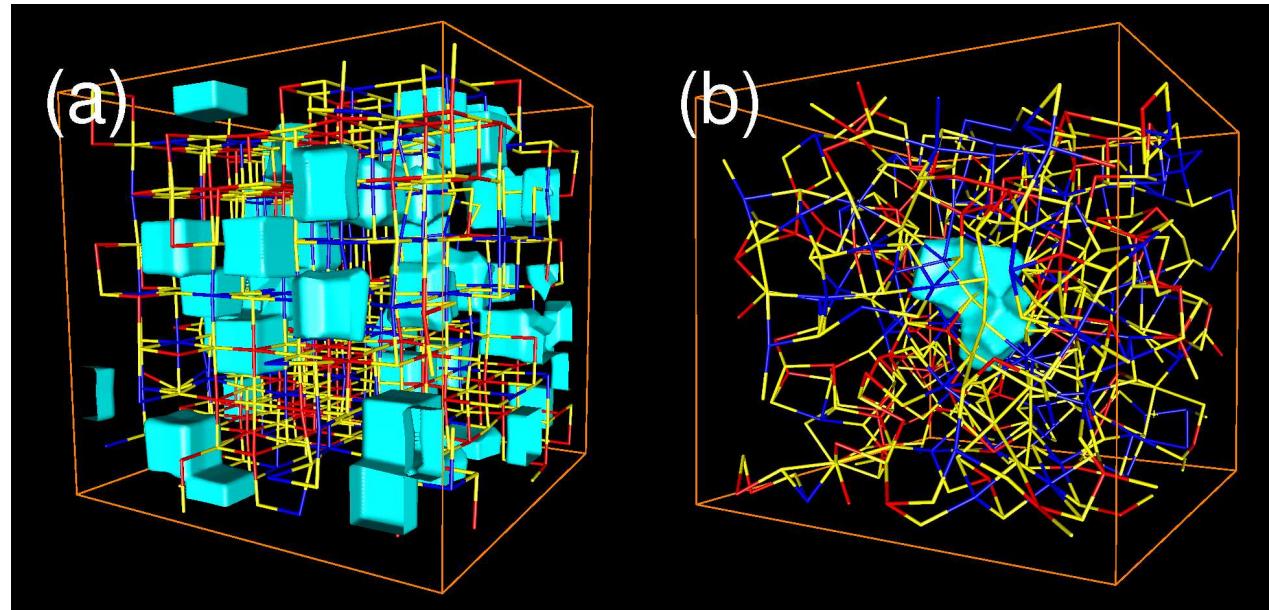


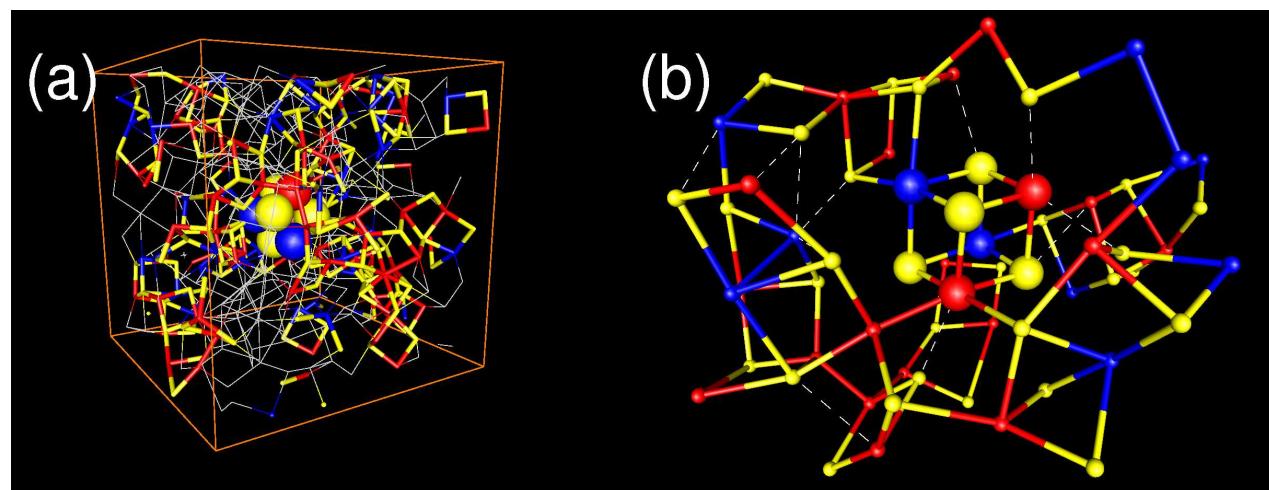
Figure 2: Statistics of irreducible n -fold ring configurations of a-GST and a-GeTe at 300 K. Black: corresponding alternating AB configurations (A : Ge/Sb, B : Te).

Rings play essential role in phase transition [cf. **S. Kohara et al.**] Appl. Phys. Lett. **89**, 201910 (2006)

Ge₂Sb₂Te₅ simulations:



Evaluate pair correlation functions, structure factors $S(Q)$, diffusion constants, order parameters,



Electronic DOS in a-GST (and c-GST):

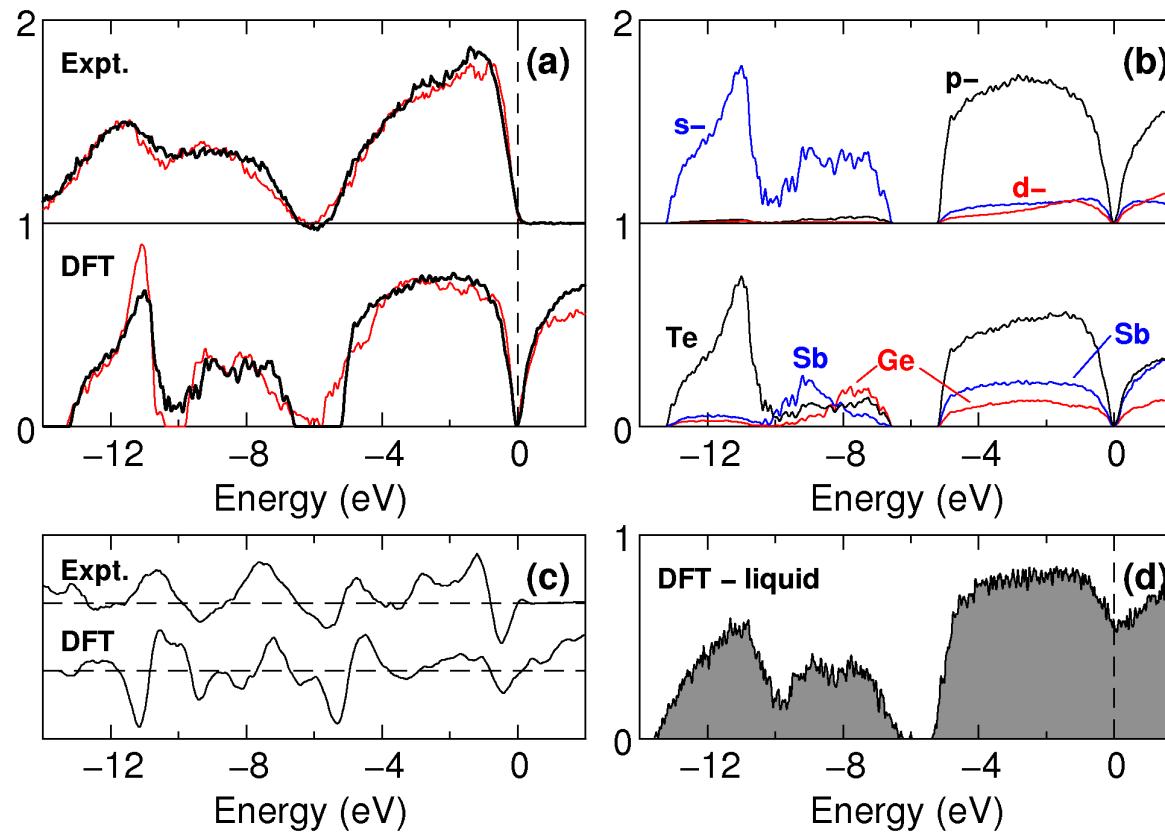
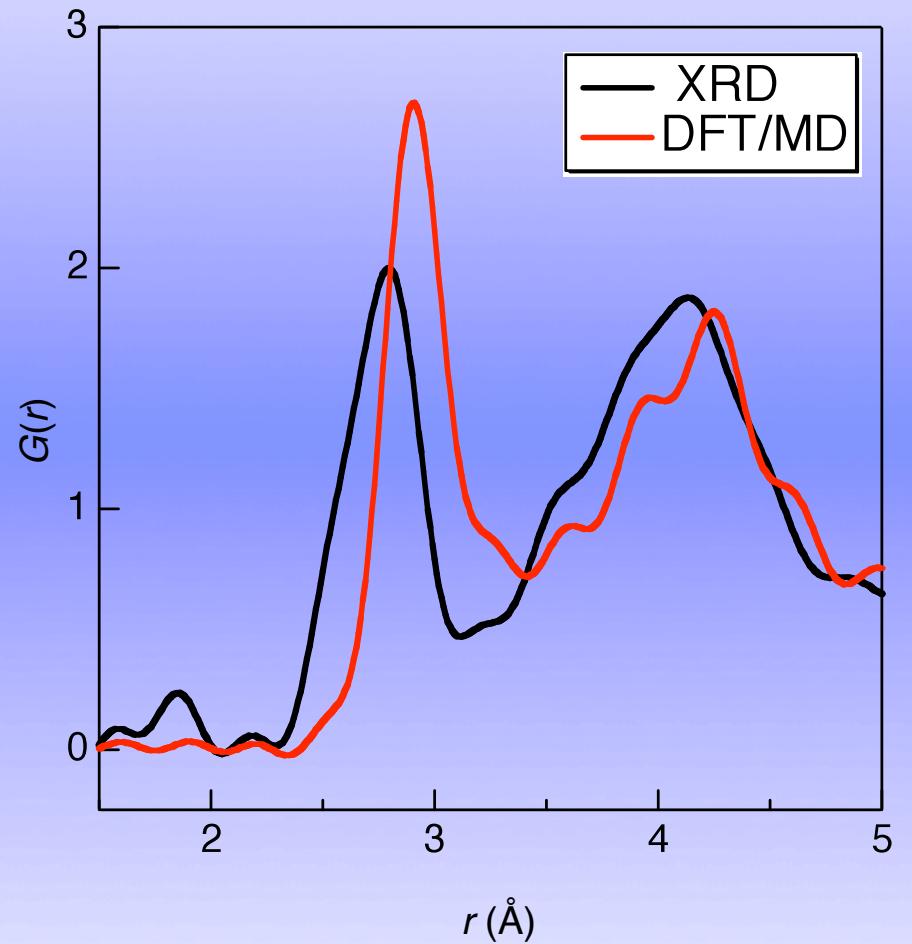
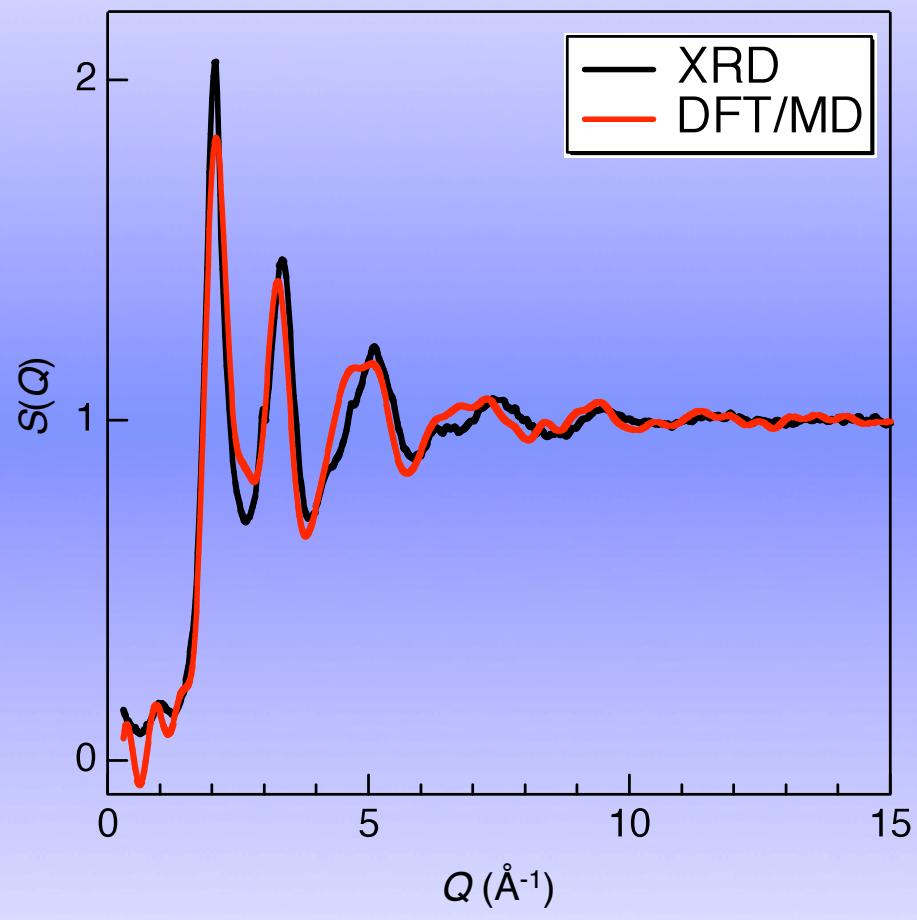


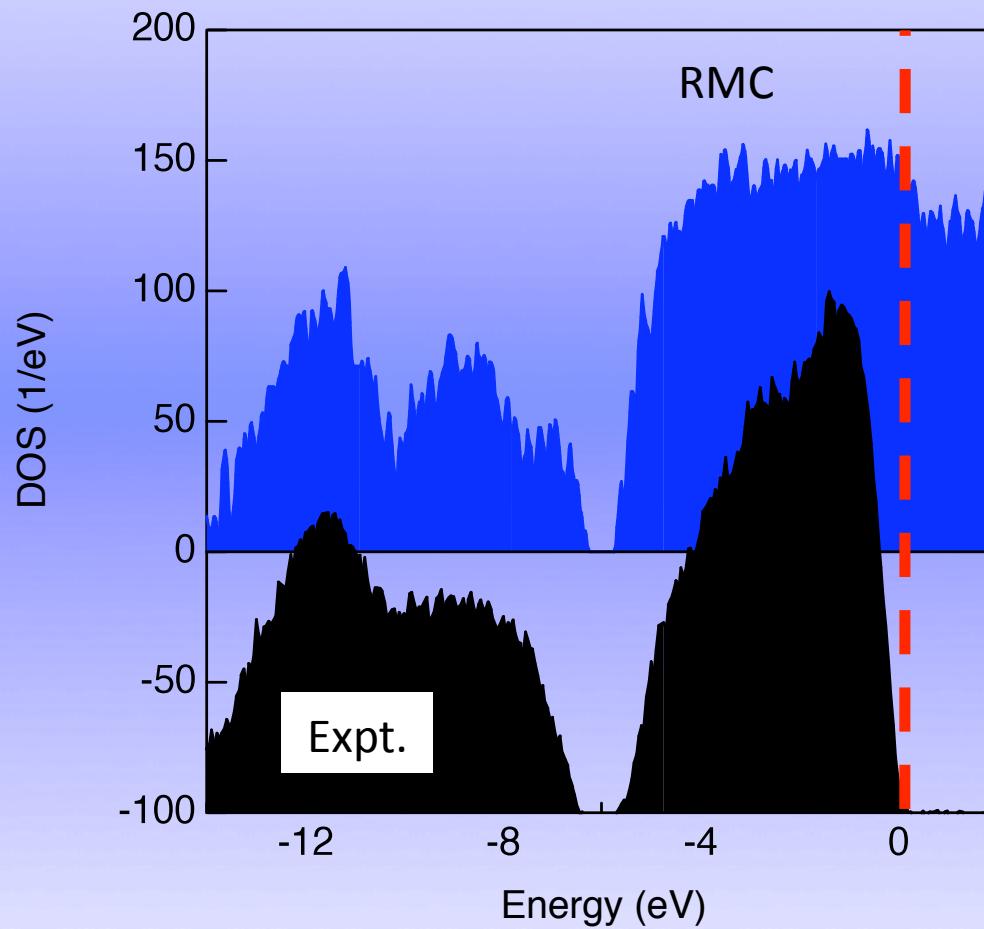
Figure 3: (a) XPS valence band spectrum of *c*- (thick black) and *a*-GST (red lines) [J.-J. Kim *et al.*, Phys. Rev. B **76**, 115124 (2007)], upper panel) and the calculated electronic DOS (lower panel). (b) Theoretical DOS of *a*-GST projected onto atom-centered *s*-, *p*-, and *d*-components and atomic types. (c) DOS difference (*a*-GST – *c*-GST, from panel (a)). (d) Electronic DOS of ℓ -GST. The vertical dashed lines mark the Fermi energy.

Problem in DFT/MD simulation



Agreement with diffraction data is insufficient

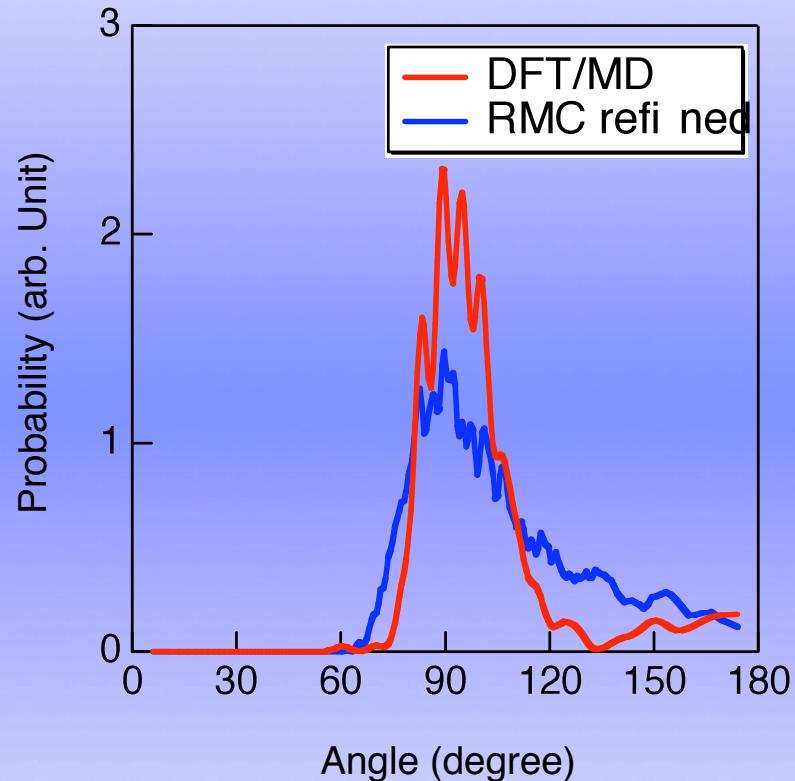
Problem in RMC simulation



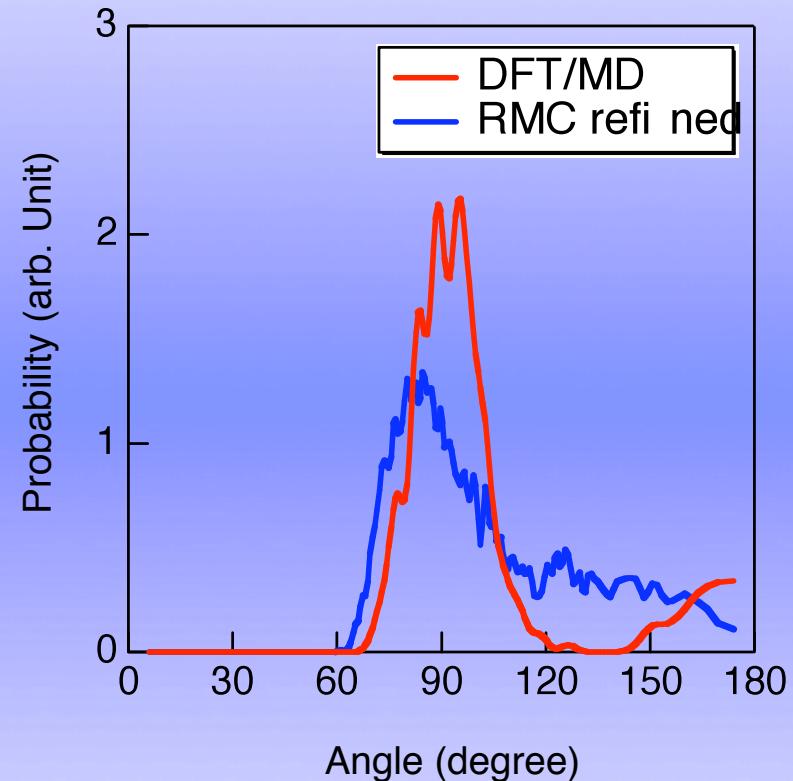
RMC model exhibits a metallic DOS

Comparison of 3-body correlations

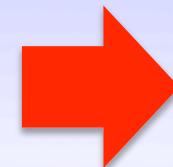
Te-Ge-Te



Te-Sb-Te

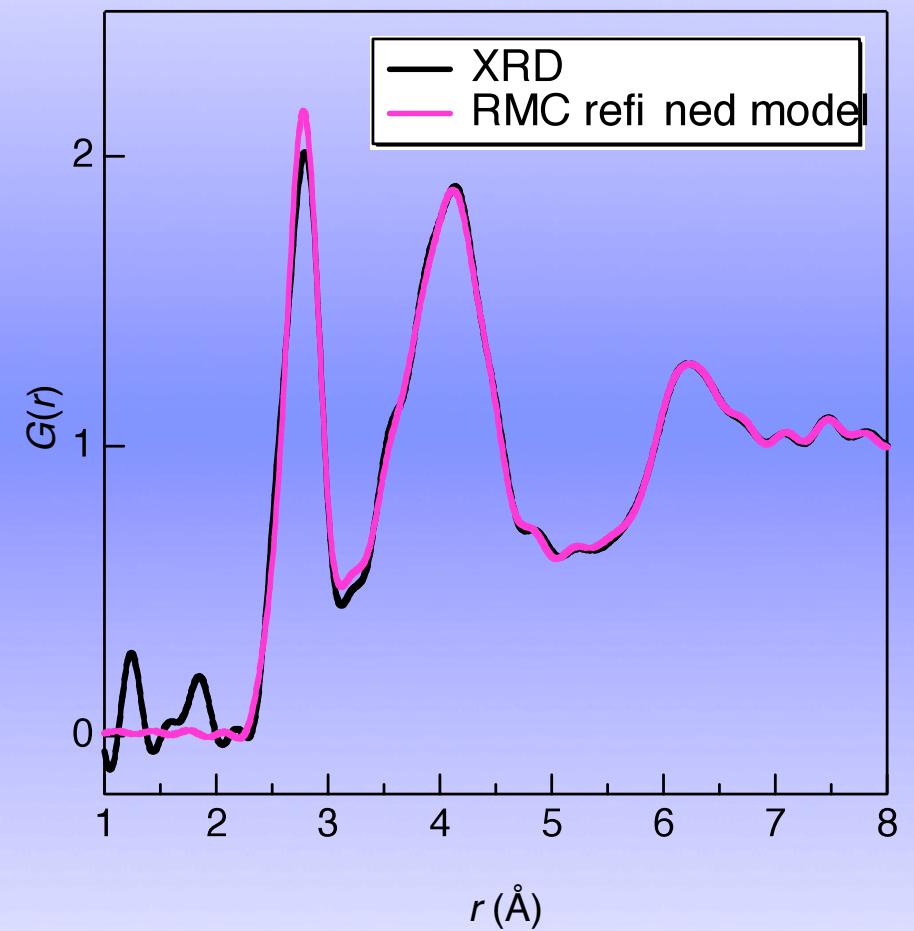
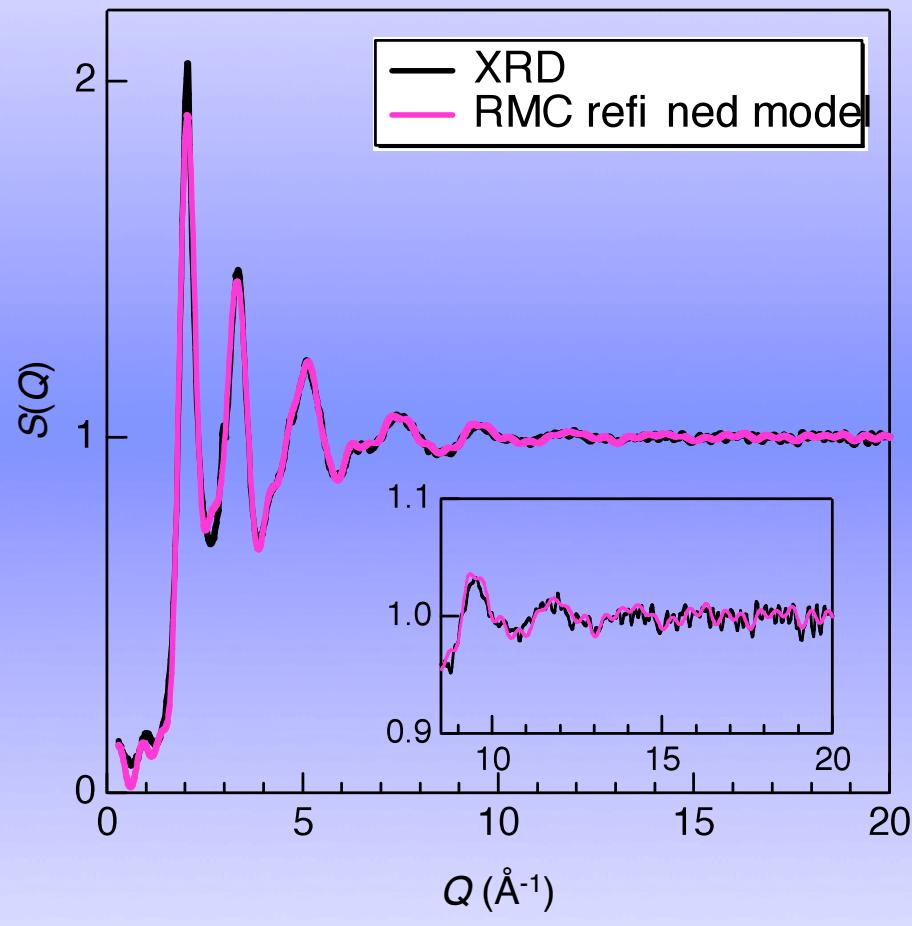


RMC refined model exhibits very broad bond angle distribution, because RMC produces the most disordered structure consistent with given diffraction data



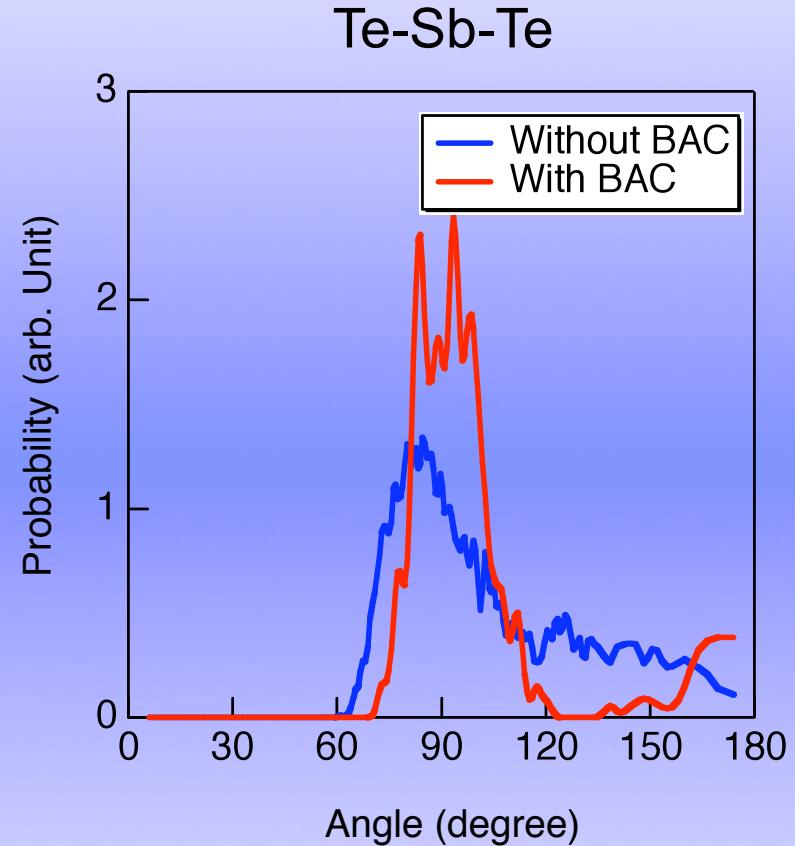
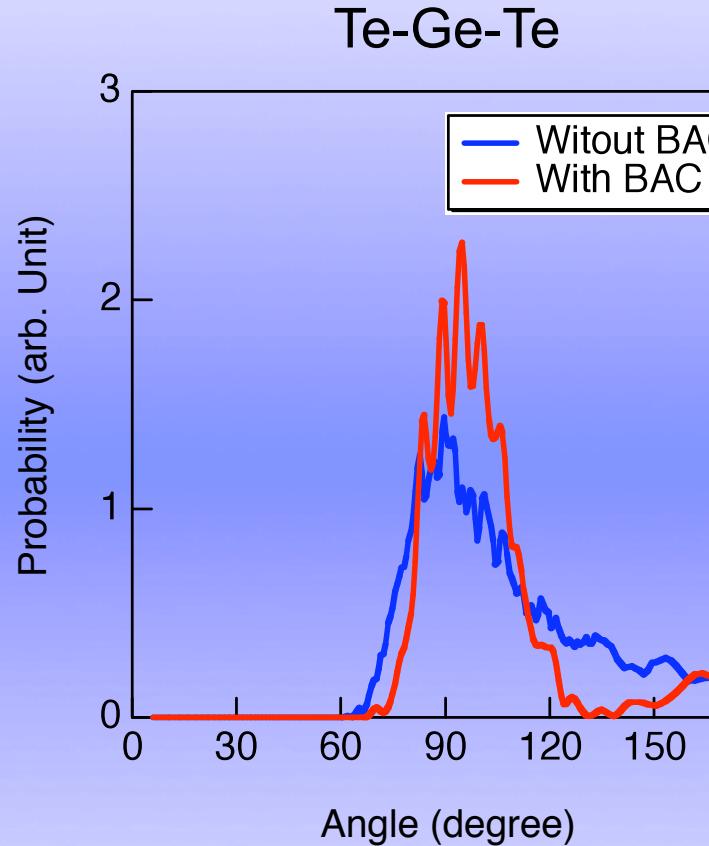
Constrains the peak width
of bond angle distributions

New RMC refined model



Agreement with diffraction data is excellent!

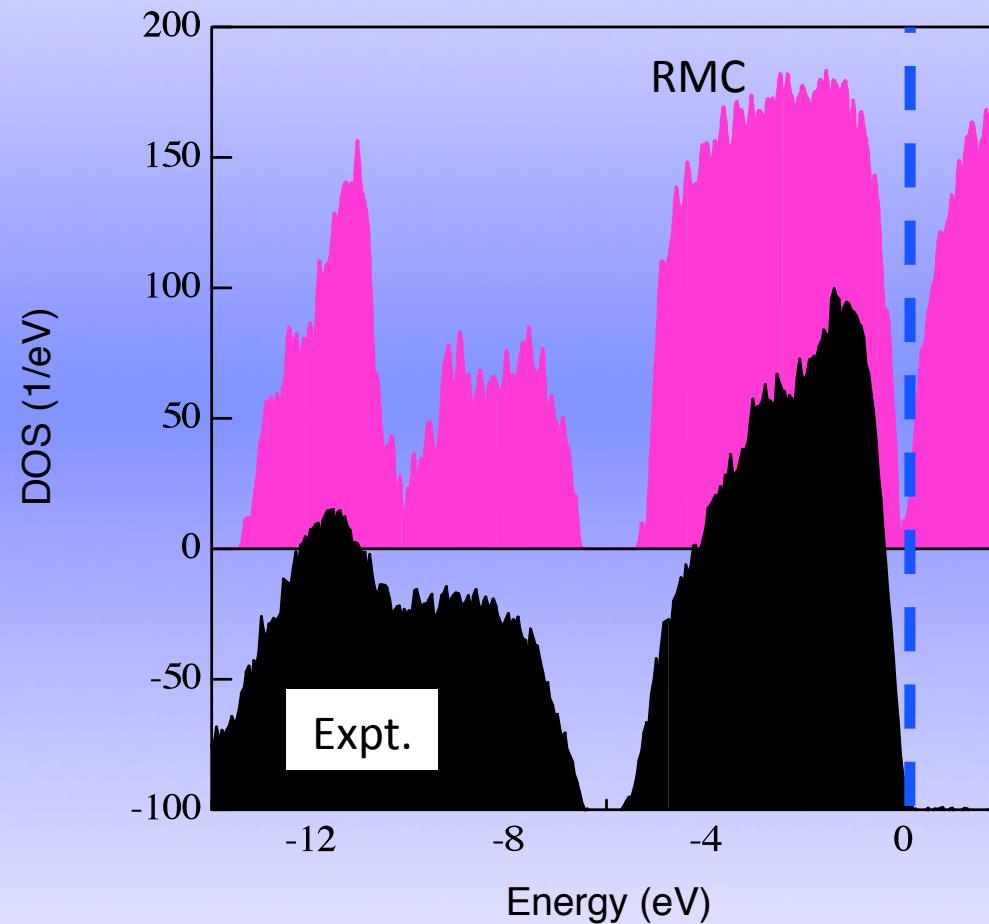
Bond angle distribution



We succeeded to constrain the peak width of bond angle distribution in the RMC refinement

BAC: Bond angle constraints

DOS of new RMC refined model



New RMC refined model
has a band gap!

Panasonic BD-RE (2010-11) $\text{Ge}_x\text{Sb}_y\text{Te}_z$: 100 GB ϕ 120 mm

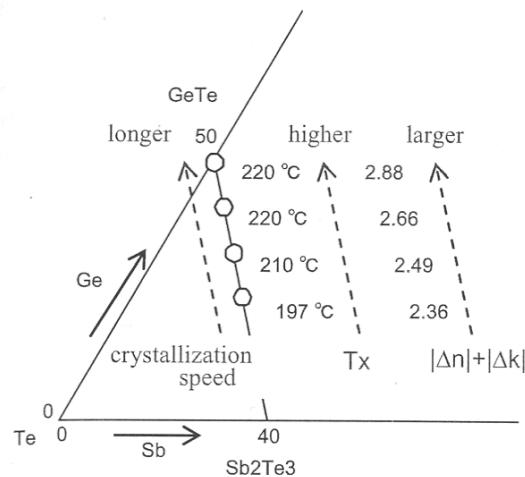


Fig. 2 Compositional dependence of phase-change properties along GeTe-Sb₂Te₃ tie line

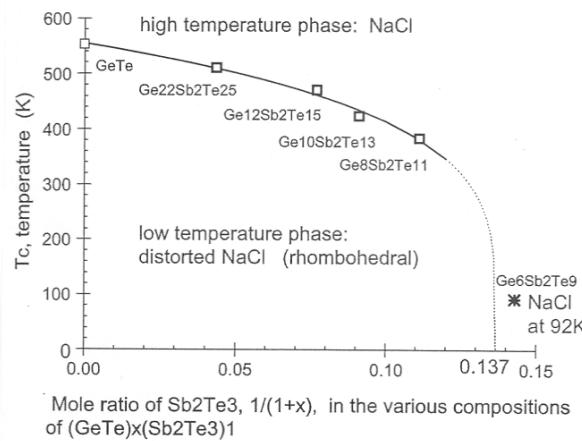


Fig. 3 Compositional dependence of crystal-crystal phase-transition temperature, T_c , on the increased Sb₂Te₃ concentration, $1/(1+x)$. (the original figure is from the reference[4].)

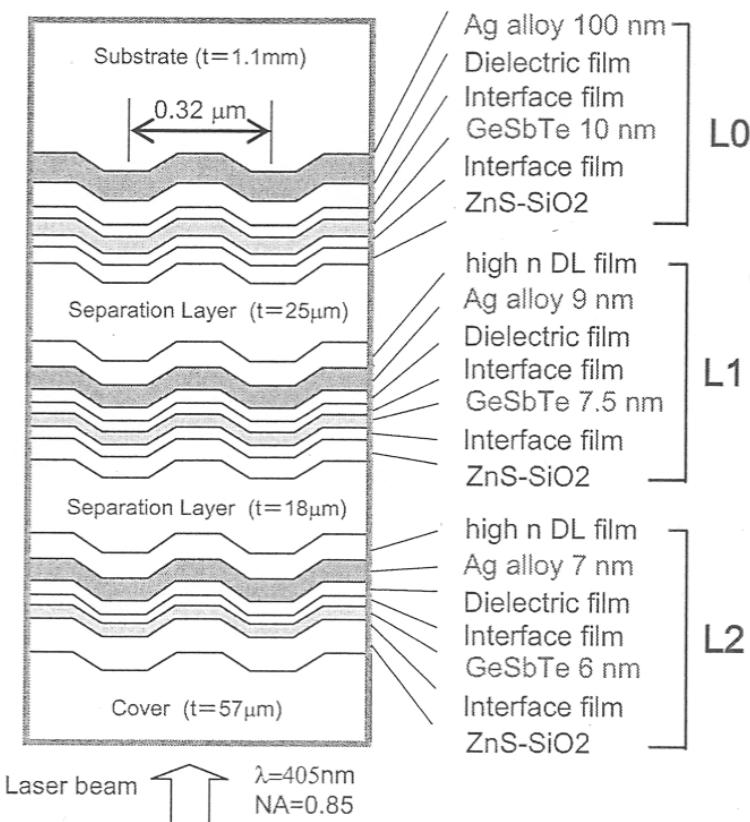
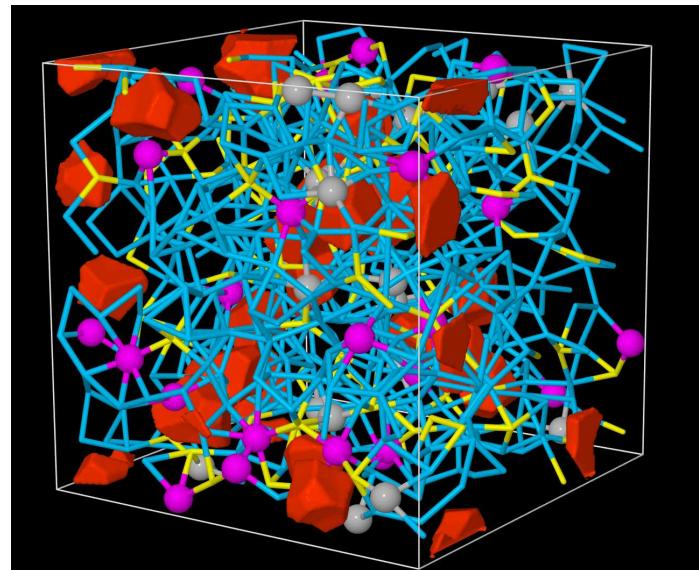


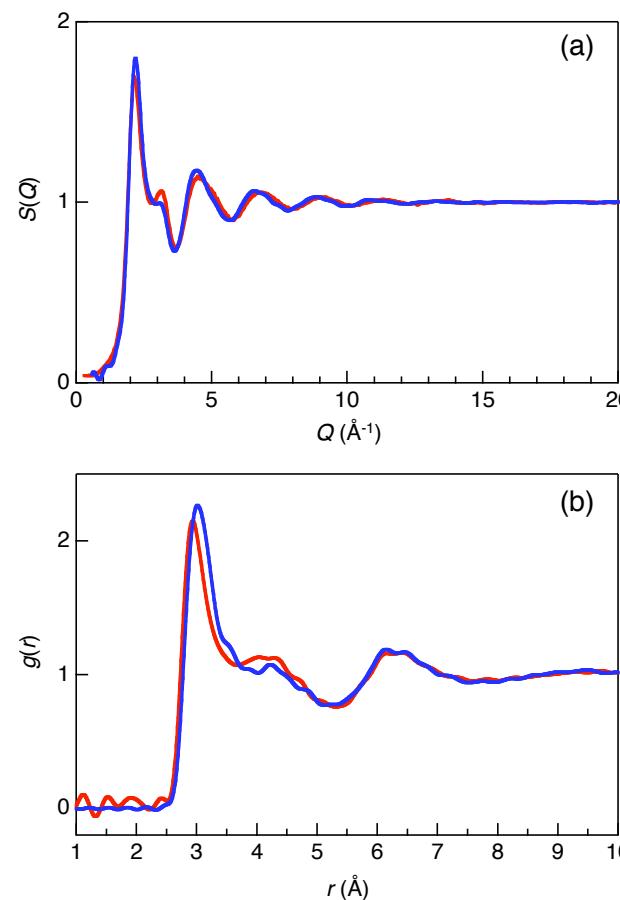
Fig. 1 Cross section of the triple layer optical disk

Liquid $\text{Ag}_{3.5}\text{In}_{3.8}\text{Sb}_{75.0}\text{Te}_{17.7}$ (AIST) simulations: (DVD-RW)



Left: (Ag: silver, In: magenta, Sb: blue, Te: yellow)

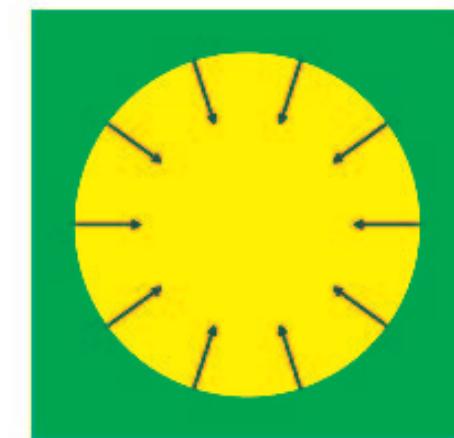
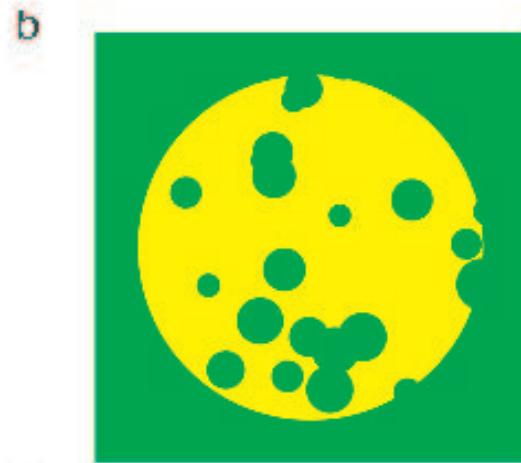
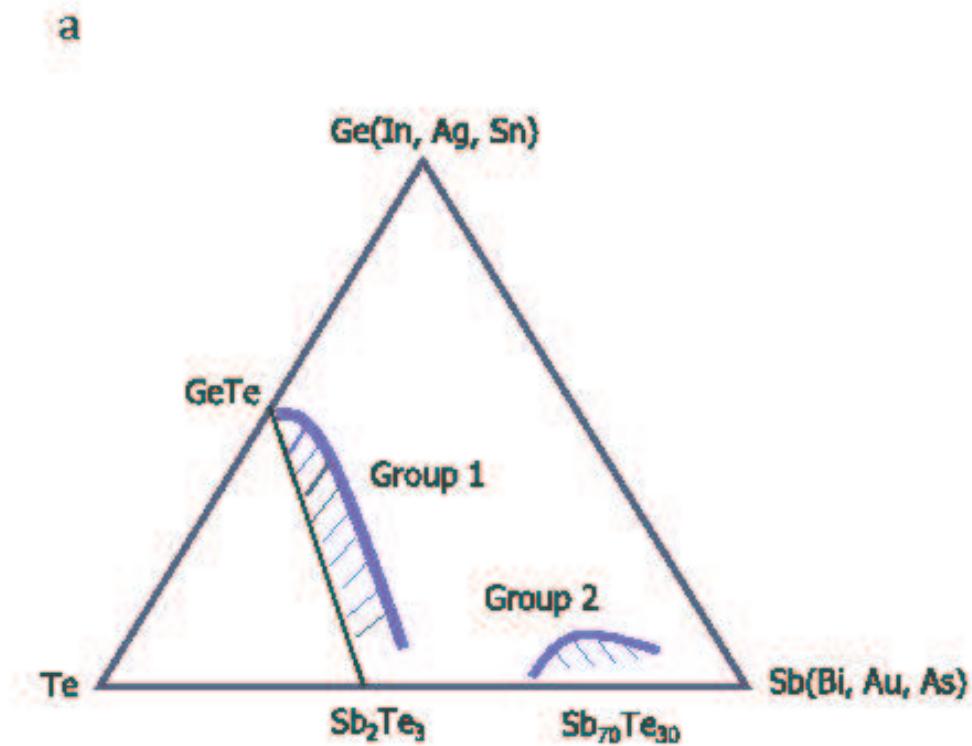
- medium-range order present
- Ag and In prefer to be near Te rather than Sb
- Ag atoms are the most mobile, have the shortest bonds and highest coordination number, and are anionic,
- In bonds to Sb and Te are longer and more flexible than those with Ag



Right: Red: XRD (862 K), Blue: MD/DF at 850 K

Two main families with different crystallization mechanisms:

Ge/Sb/Te (GST) and doped Sb/Te (near eutectic) alloys



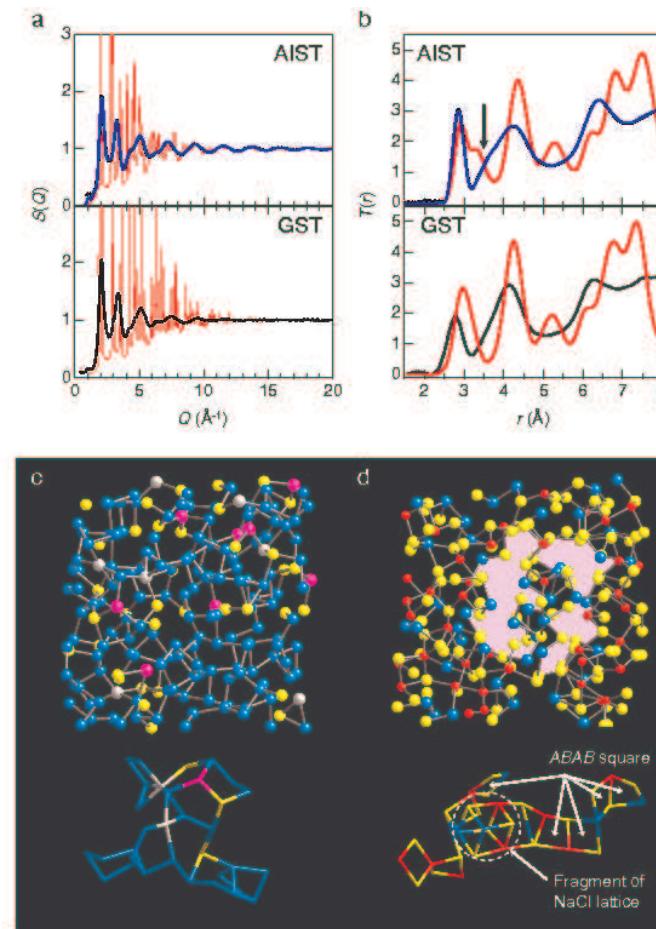
GST: nucleation from inside bit

AIST: growth from crystalline surroundings

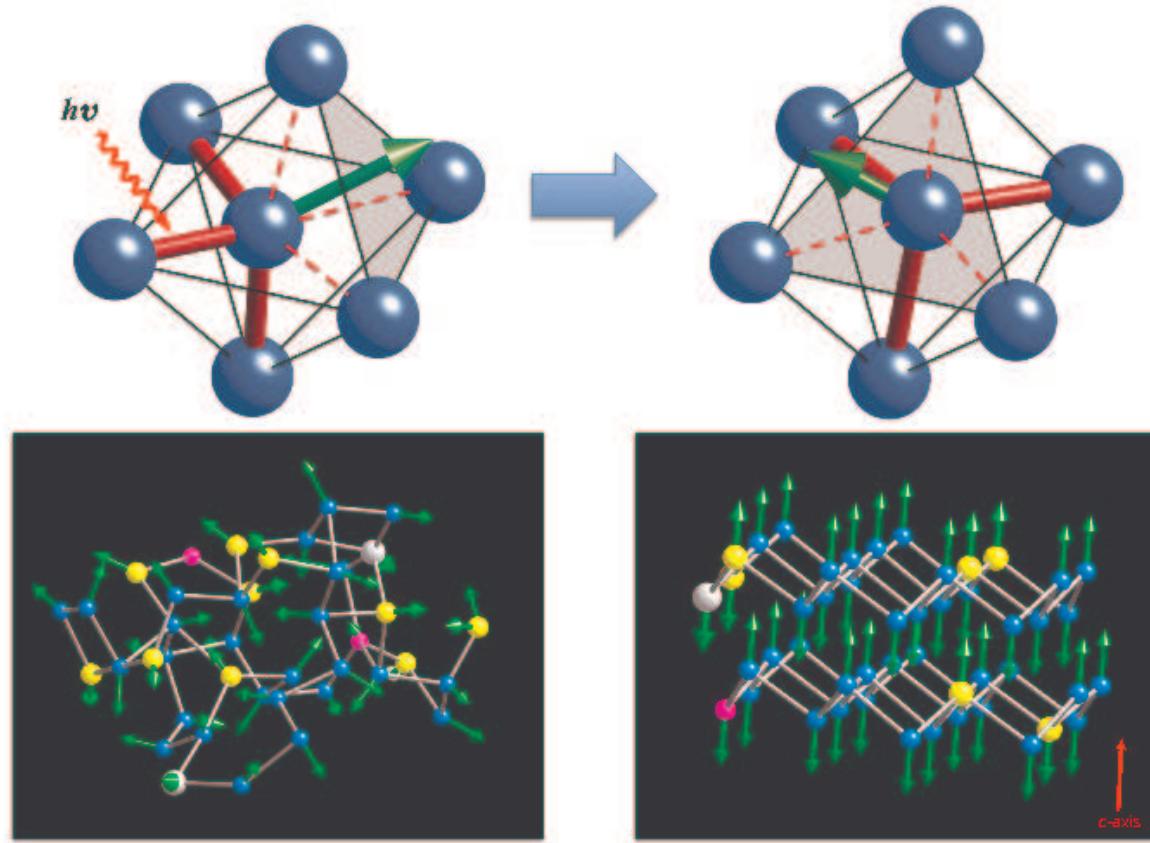
AIST Simulations: 640 atoms, ca. 200 ps

Experimental: XRD, EXAFS, XPS (SPring-8)

T. Matsunaga et al. *Nature Materials* DOI: 10.1038/NMAT2931 (online 9 January 2011)

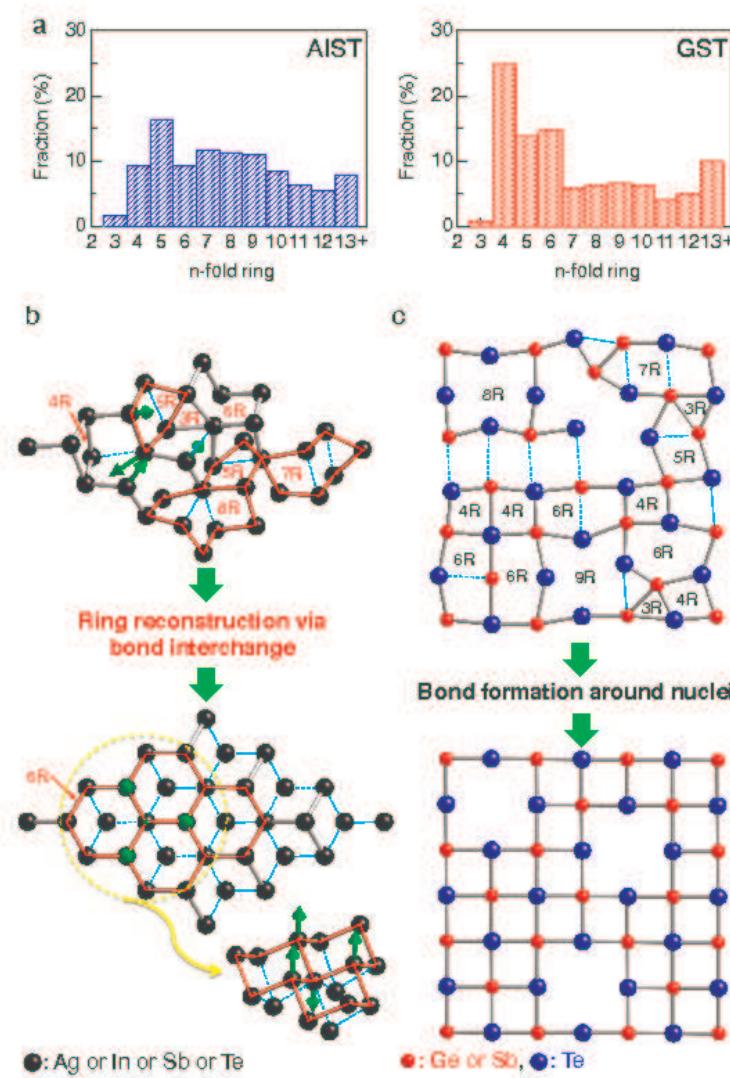


Proposed crystallization mechanism in AIST:



Bond exchange model: exchange of short Sb-Sb bonds with longer Sb-Sb bonds

Differences between crystallization in GST and AIST families:



Progress:

- Identification of basic structural unit in GST, GeTe, .. (“ $ABAB$ squares”)
- Order (medium- to long-range) in “disordered” materials (Te, cavities)
- Vibrational and electronic structure
- Eutectic structure ($\text{Ge}_{15}\text{Te}_{85}$): Corner and edge-sharing GeTe_4 units
- Role of cavities
- $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ Blu-ray Disc (BD) [630 atoms], remarkable similarities to $\text{Ge}_2\text{Sb}_2\text{Te}_5$
- Need “large” simulations (identify “order”, role of cavities, ..)
- Need “long” simulations (increasing order, decreasing number of “wrong bonds”, AIST (DVD-RW) [640 atoms, liquid, amorphous] “Bond exchange” model
- Comparison of “as-deposited” and “melt-quenched” structures [Phys. Rev. B (2011, accepted)]

Other systems:

- Te (with several functionals) [343 atoms]
J. Akola, R. O. Jones, S. Kohara, T. Usuki, E. Bychkov, Phys. Rev. B **81**, 094202 (2010)
- Role of different functionals: PBE, PBEsol, TPSS, ...