Charge Density Wave Materials: Superstructures in Polytelluride Compounds with Square Nets

Peierls distortions and charge density waves as band-gap forming mechanisms

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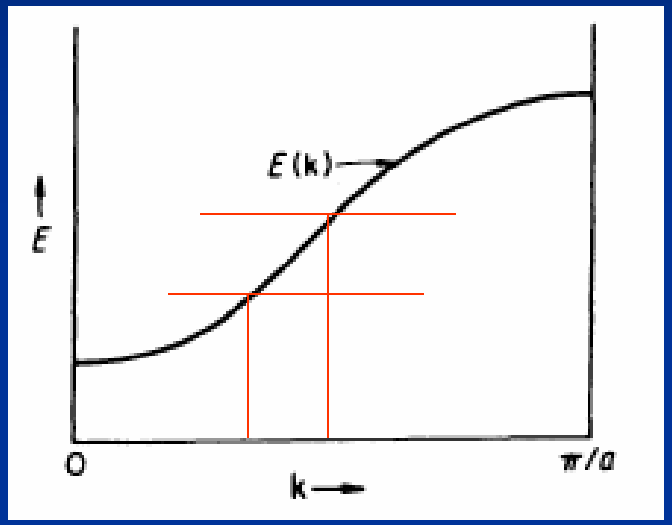
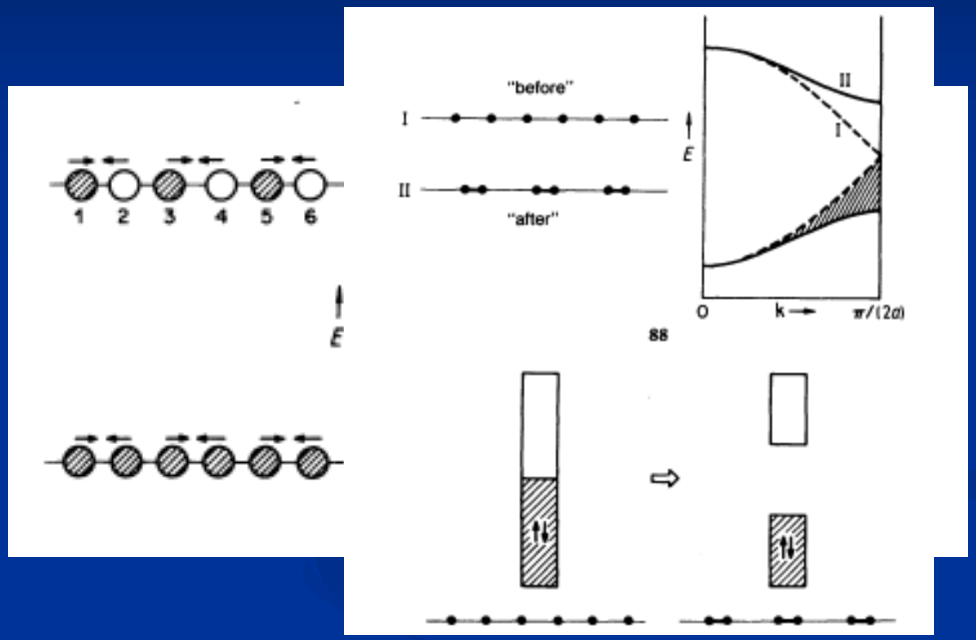
Simon Billinge, Hyun Jeong Kim
and Mercouri G Kanatzidis

2010

Peierls Distortion
one-dimensional system



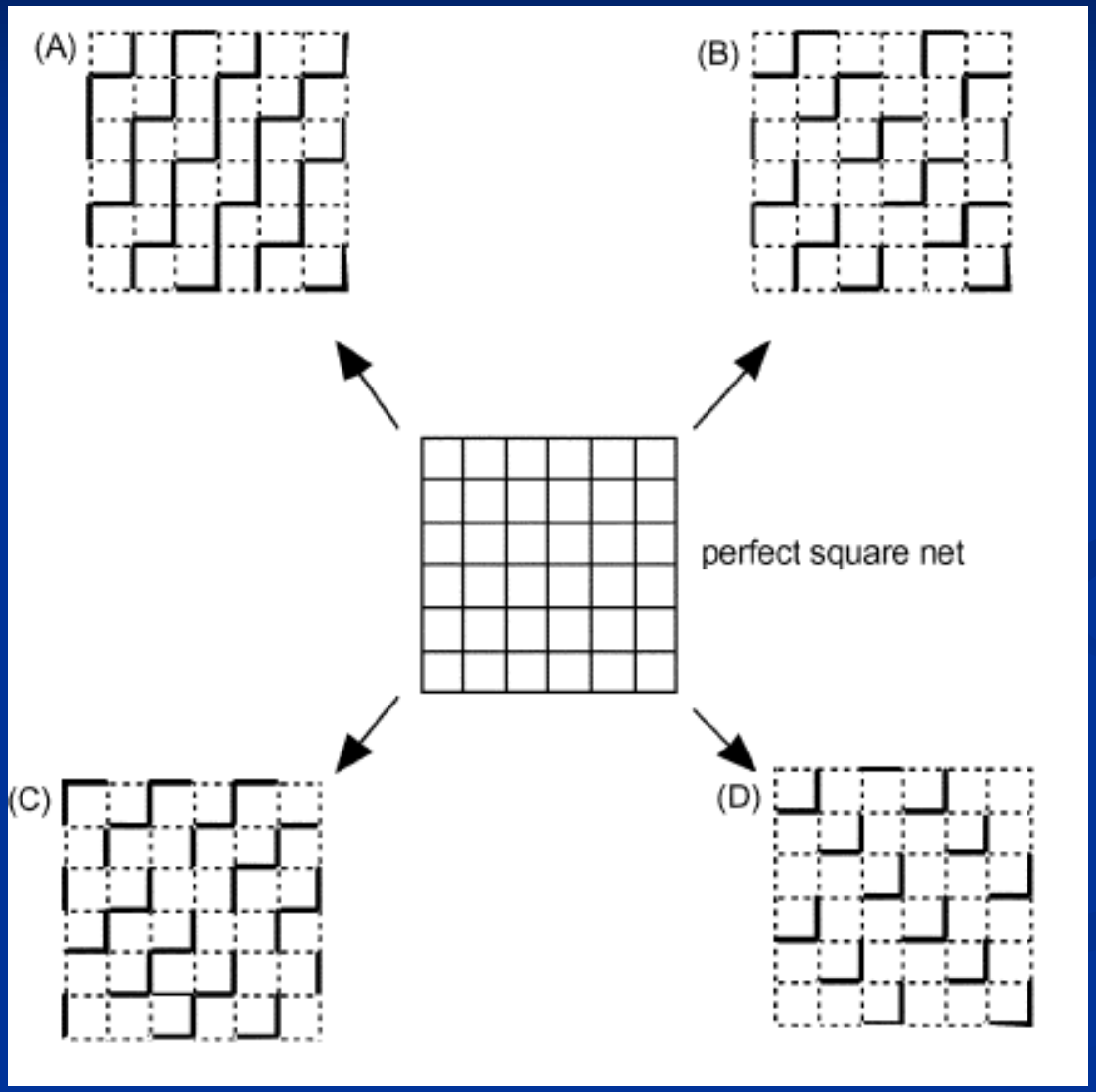


Half-filled band unstable…

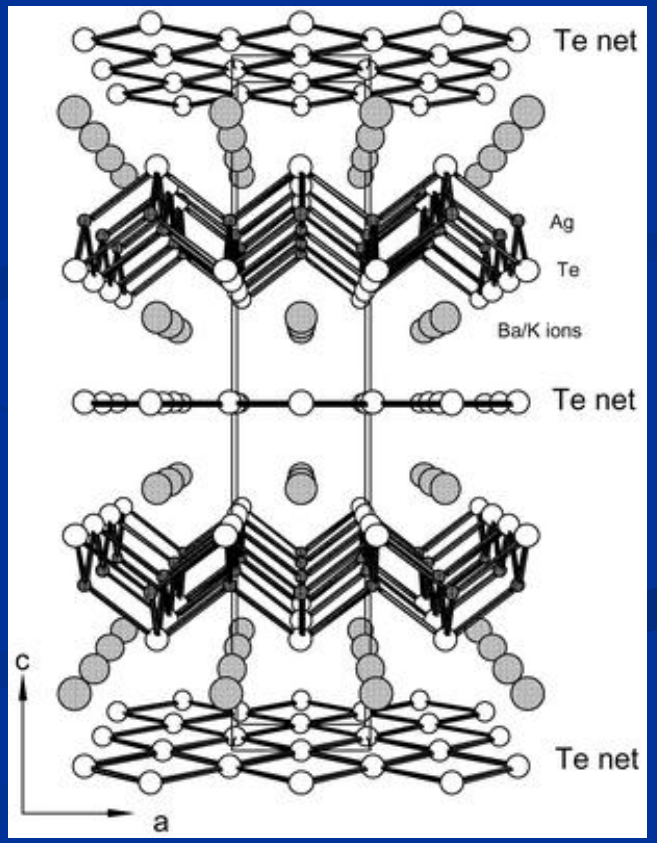
Opens energy gap

Solids and **Surfaces**: A Chemist's View of Bonding in Extended Structures.
Roald Hoffmann

Peierls distortion two-dimensional system



Examples:
Many tellurides, antimonides
Silicides etc $K_{0.33}Ba_{0.66}AgTe_2$

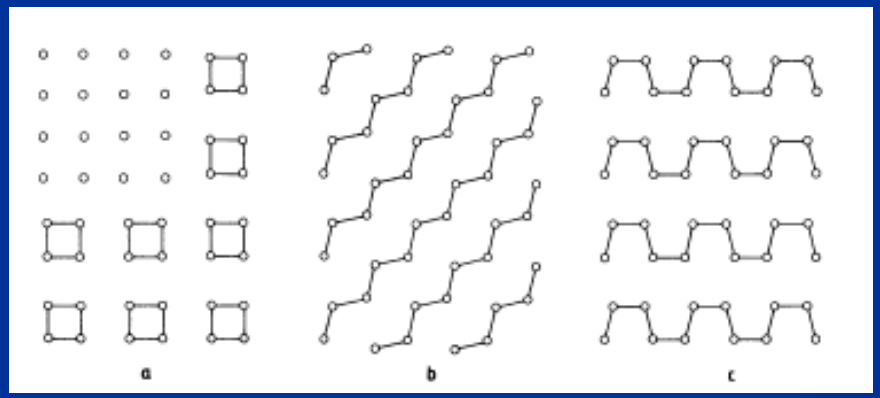


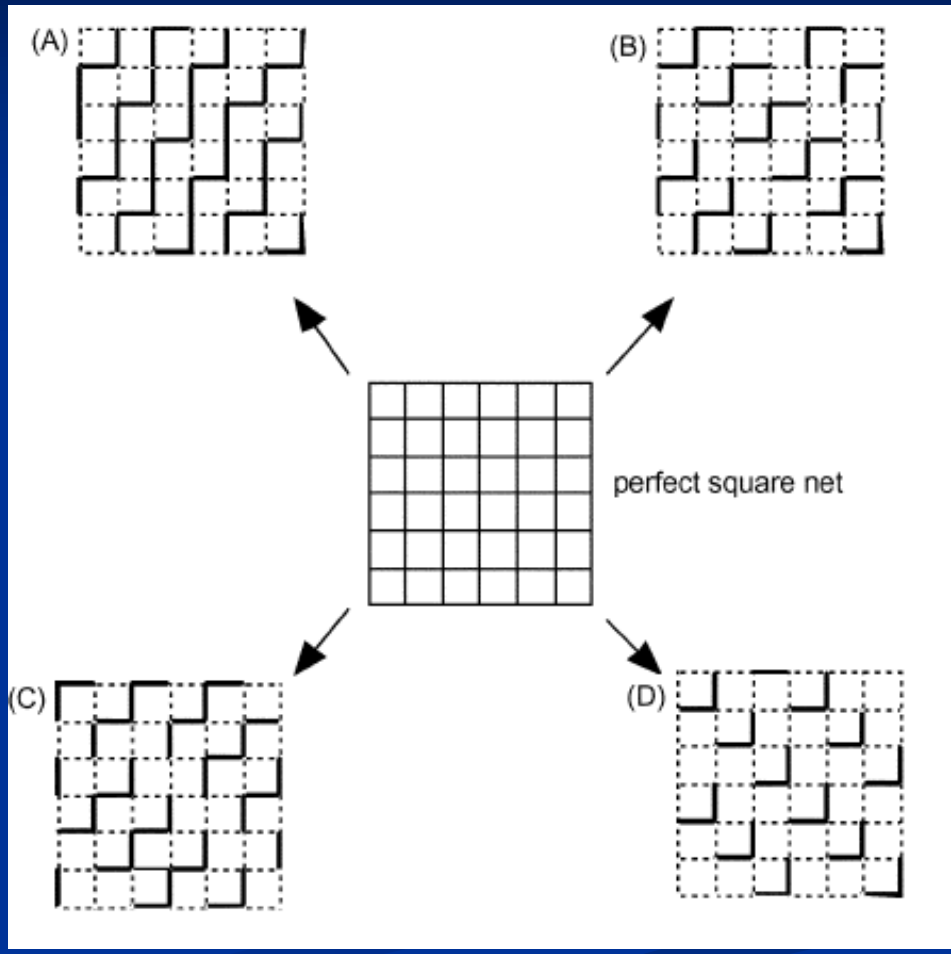
Net distortions

Structural distortions in the Te net lower the energy of the Te p-orbitals and localize the electron density into the fully occupied bonding orbitals.

A gap opens up at the Fermi Level: **Metal-Insulator or Metal-poor metal transition**

Te^0

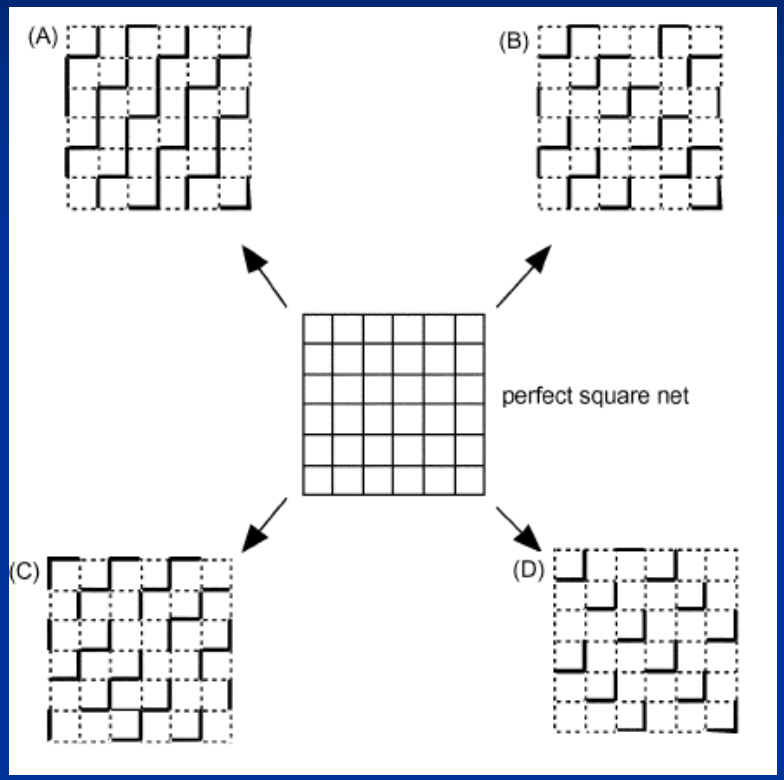




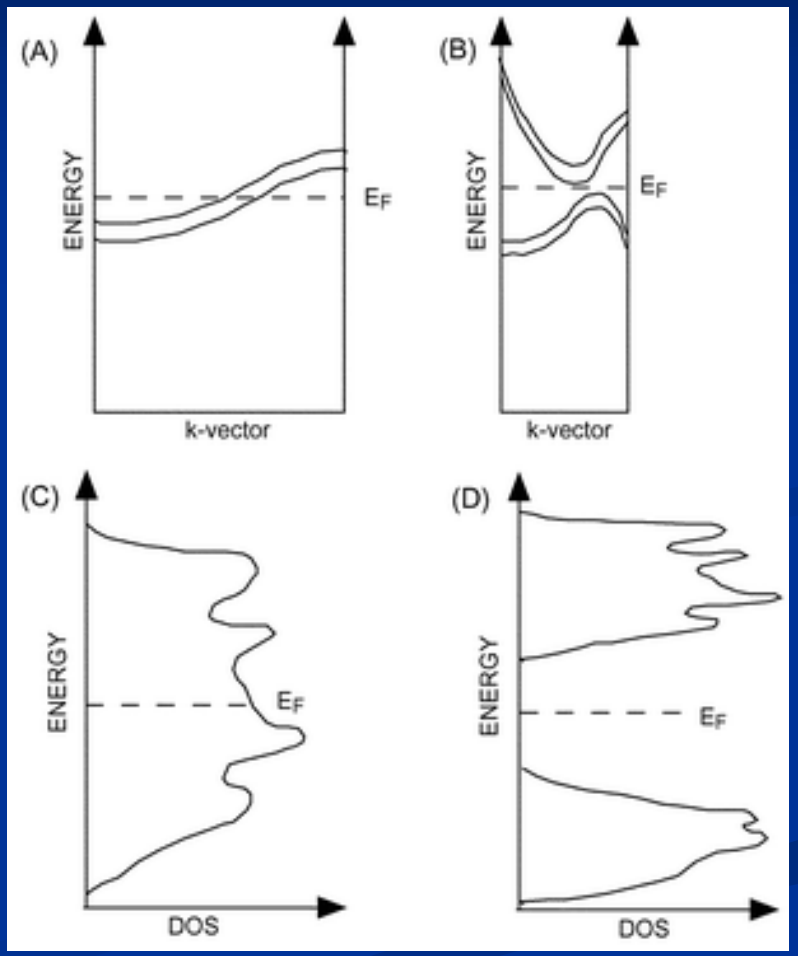
Charge/Te atom: -2, -1, -½, -⅓, etc

Kanatzidis and Patschke, *Phys Chem Chem Phys*, **2002**, 4, 3266

Charge density waves (CDW). Electron phonon coupling



large displacements of the atoms cause the atomic coordination to be reduced



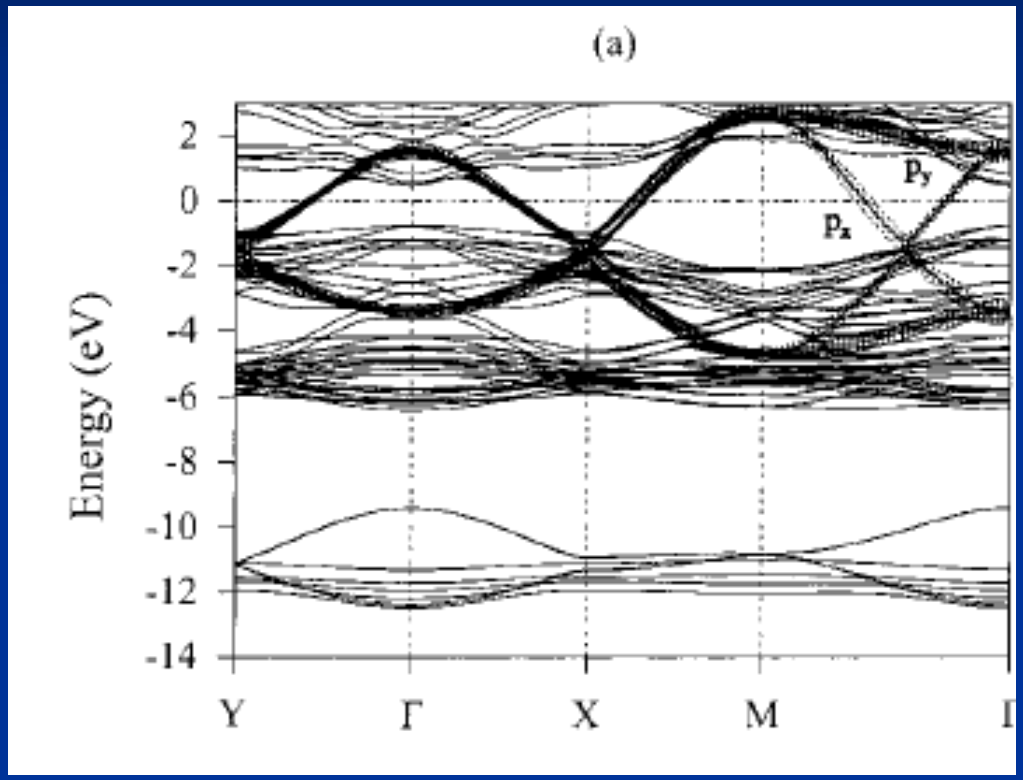
Charge/Te atom: -2, -1, -½, -⅓, etc

Competition between superconductitivy and CDW distortion

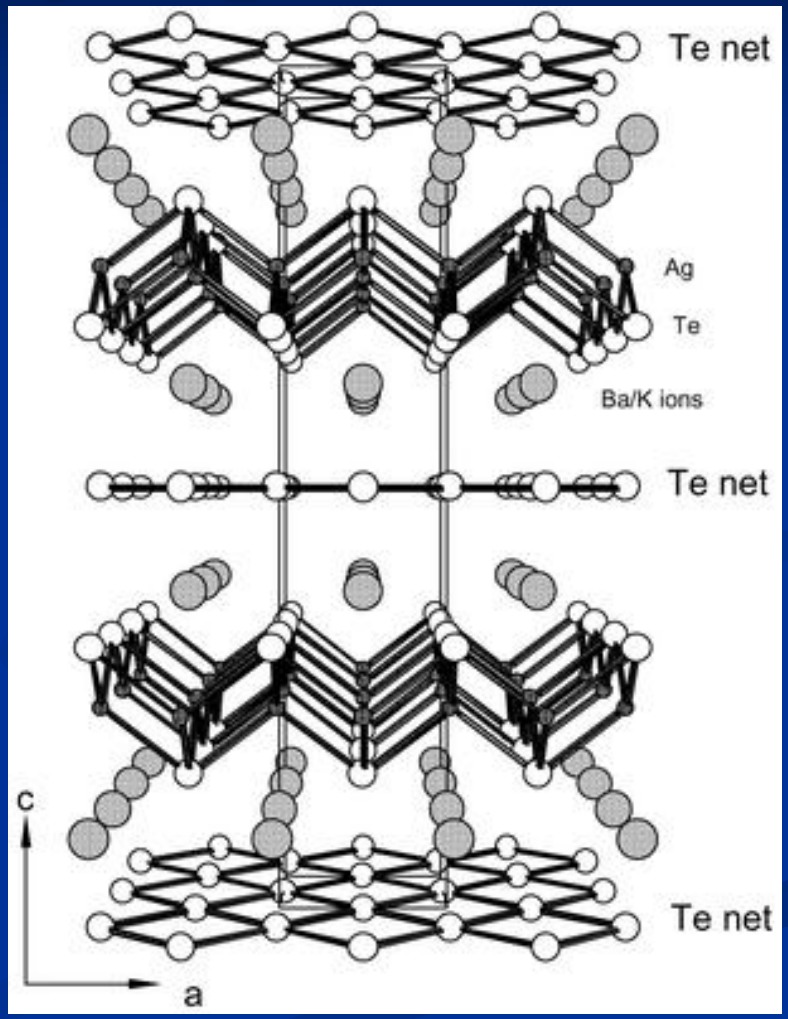
Mechanism for forming very narrow gap semiconductors

- Narrow gap semiconductors are of interest as long wavelength detector materials and thermoelectrics
- PbTe 0.28 eV, Bi_2Te_3 0.14 eV, $CsBi_4Te_6$ 0.08 eV, $(Bi_{0.8}Sb_{0.2})$ 0.03 eV.
- Very narrow gaps (<0.05 eV) are very difficult to design.
  - may be possible with CDW systems arising from square nets of e.g. Te.

$K_{0.33}Ba_{0.66}AgTe_2$



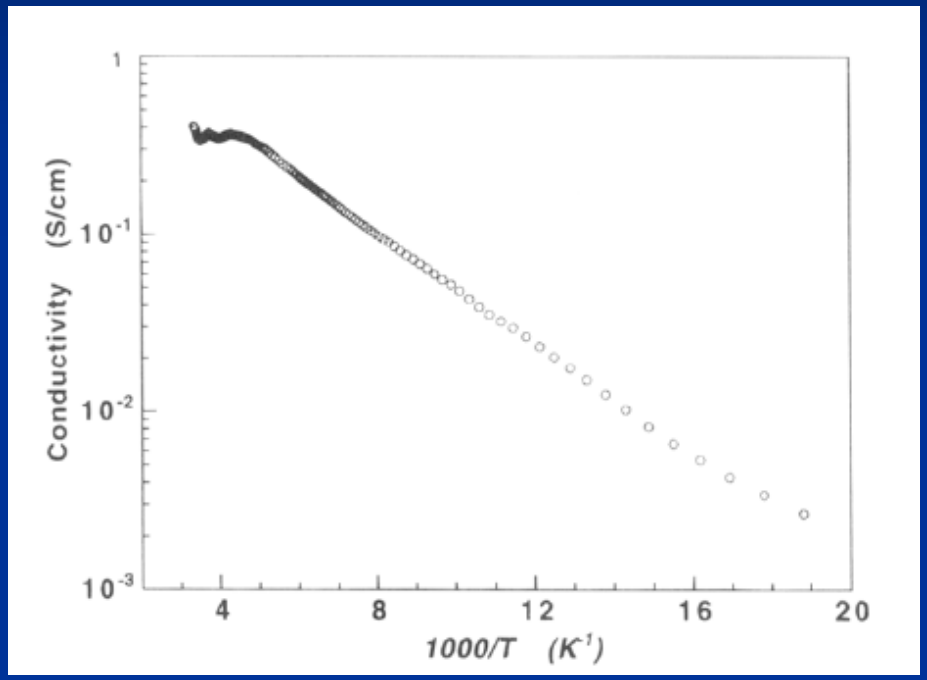
Metallic!



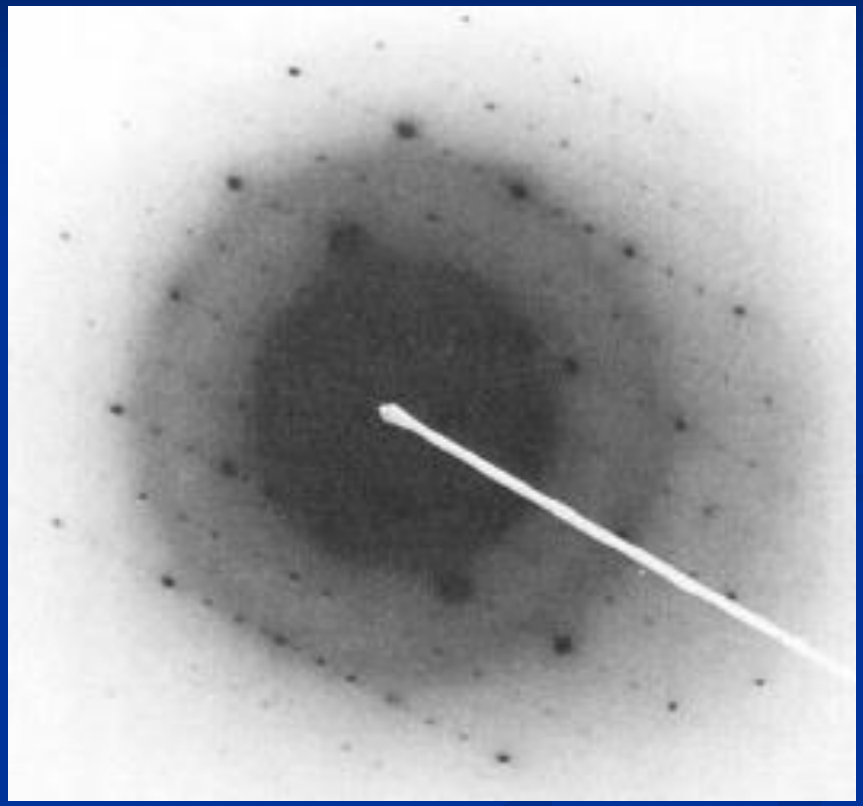
I 4/mmm

J. Li, S. Lee, M. G. Kanatzidis, *J. Am. Chem. Soc.* 1995

Electrical properties and superstructure

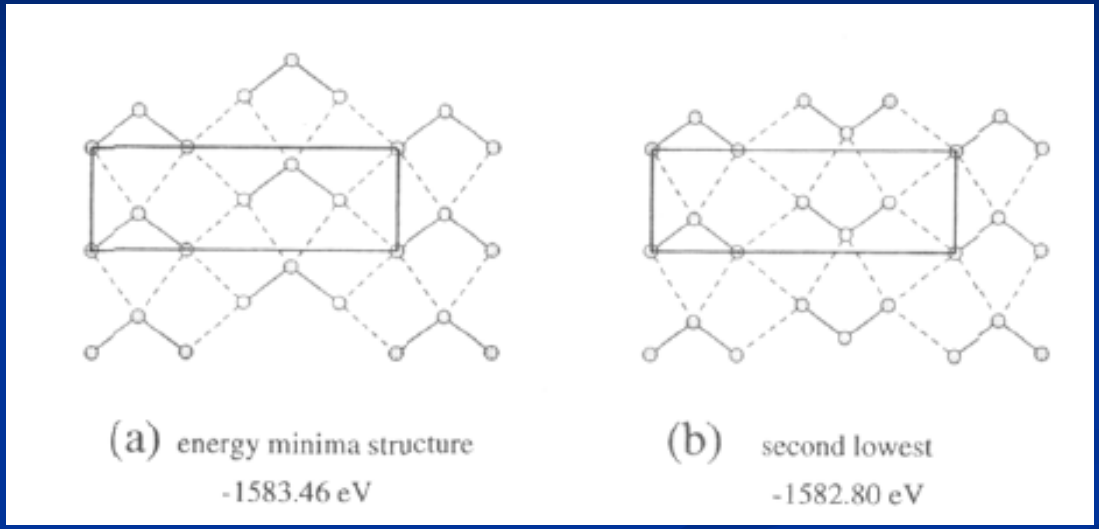


Semiconductor…



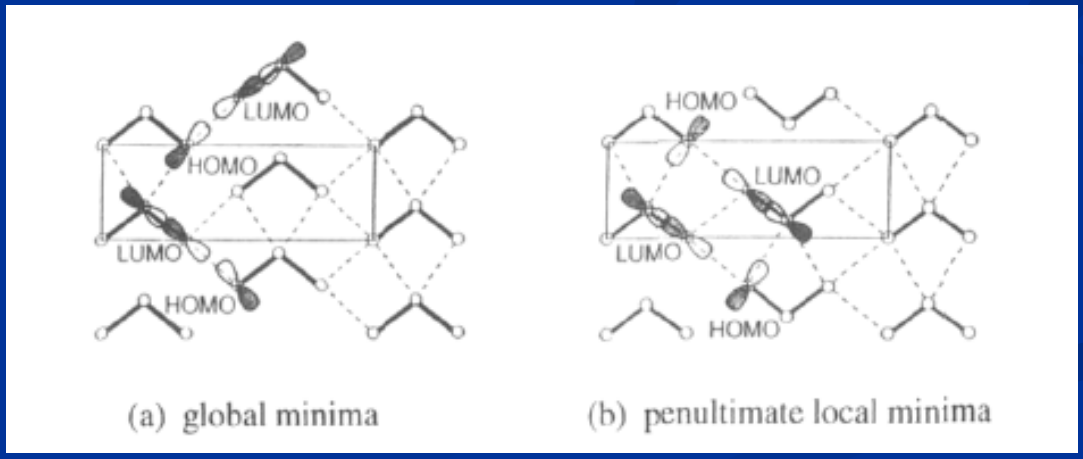
$[K_{0.33}Ba_{0.66}]^{1.66+}(AgTe)^{+}Te^{-0.66}$
Predicts Te_3^{2-}

Trimers $(Te_3)^{2-}$, bonding (proposed)



(a) energy minima structure
-1583.46 eV

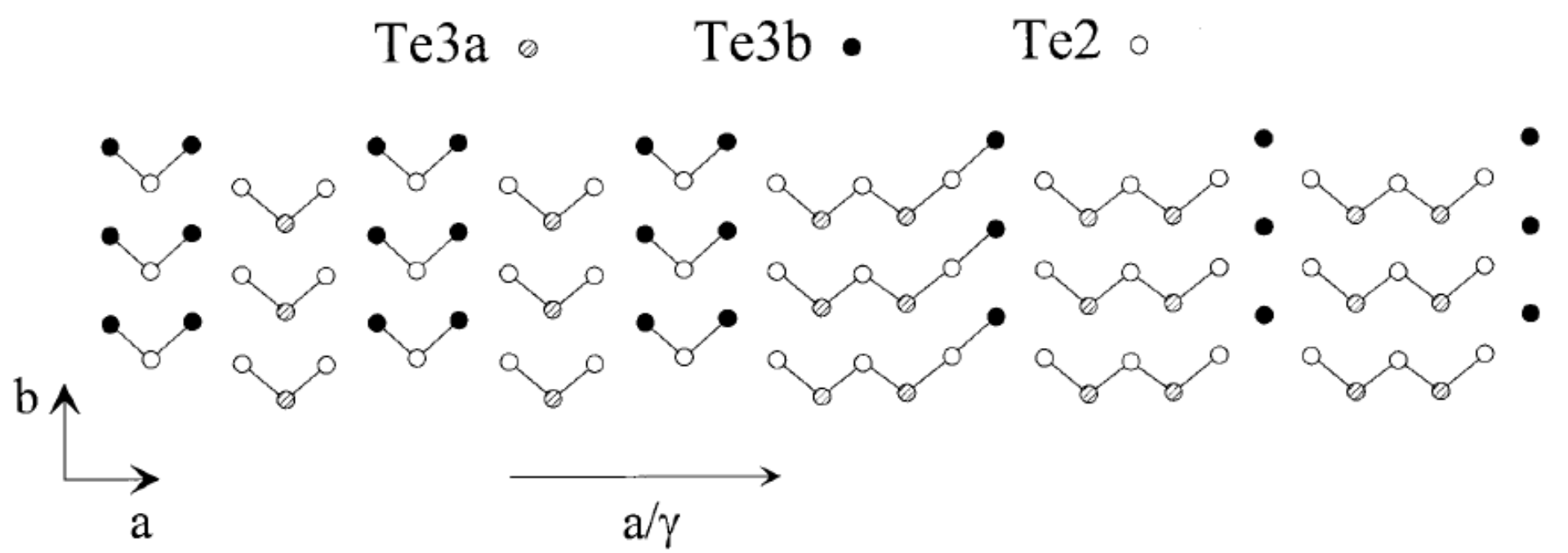
(b) second lowest
-1582.80 eV



(a) global minima

(b) penultimate local minima

Distortion pattern in $K_{0.33}Ba_{0.66}AgTe_2$

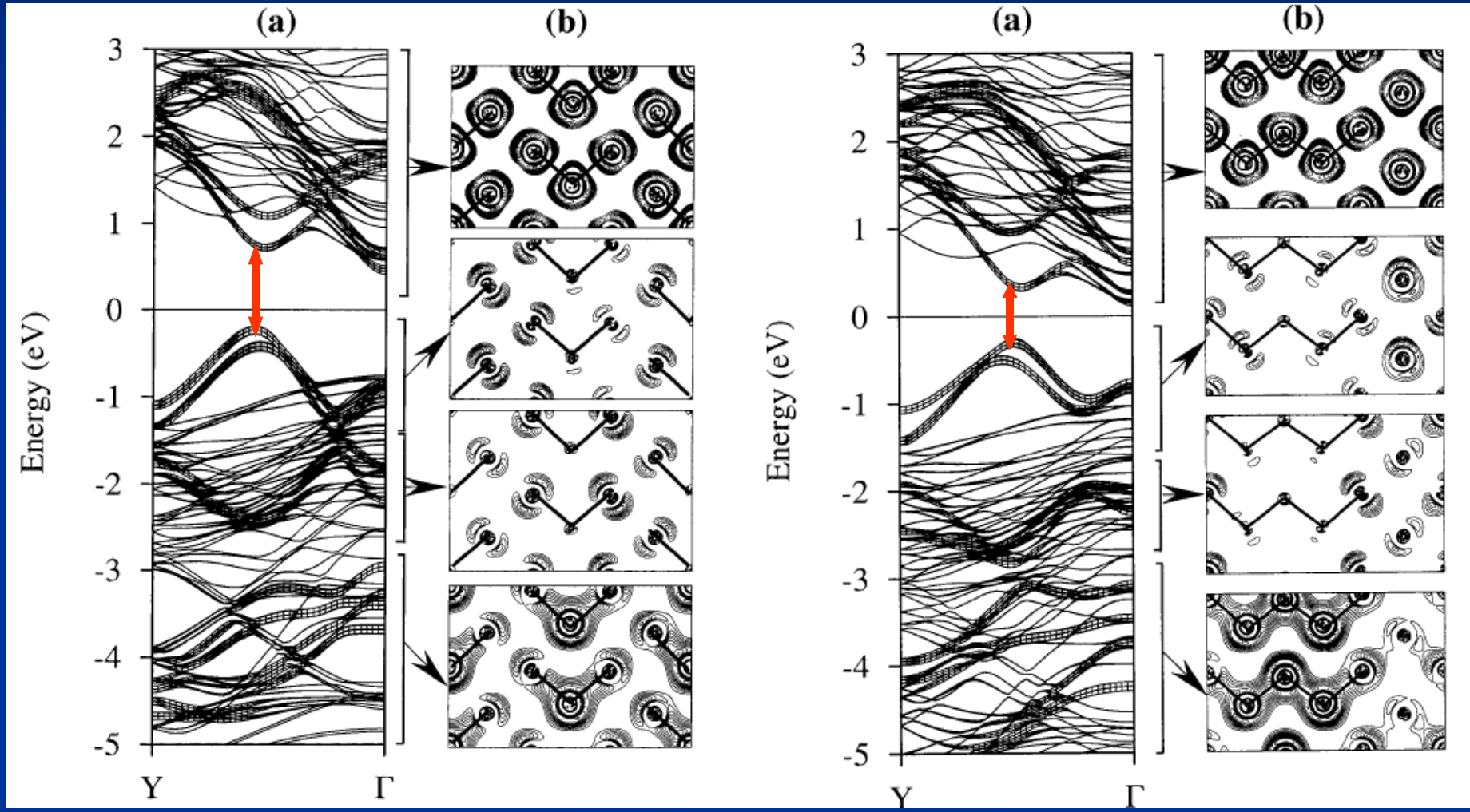


$Te^{-0.66}$ or Te_3^{2-}

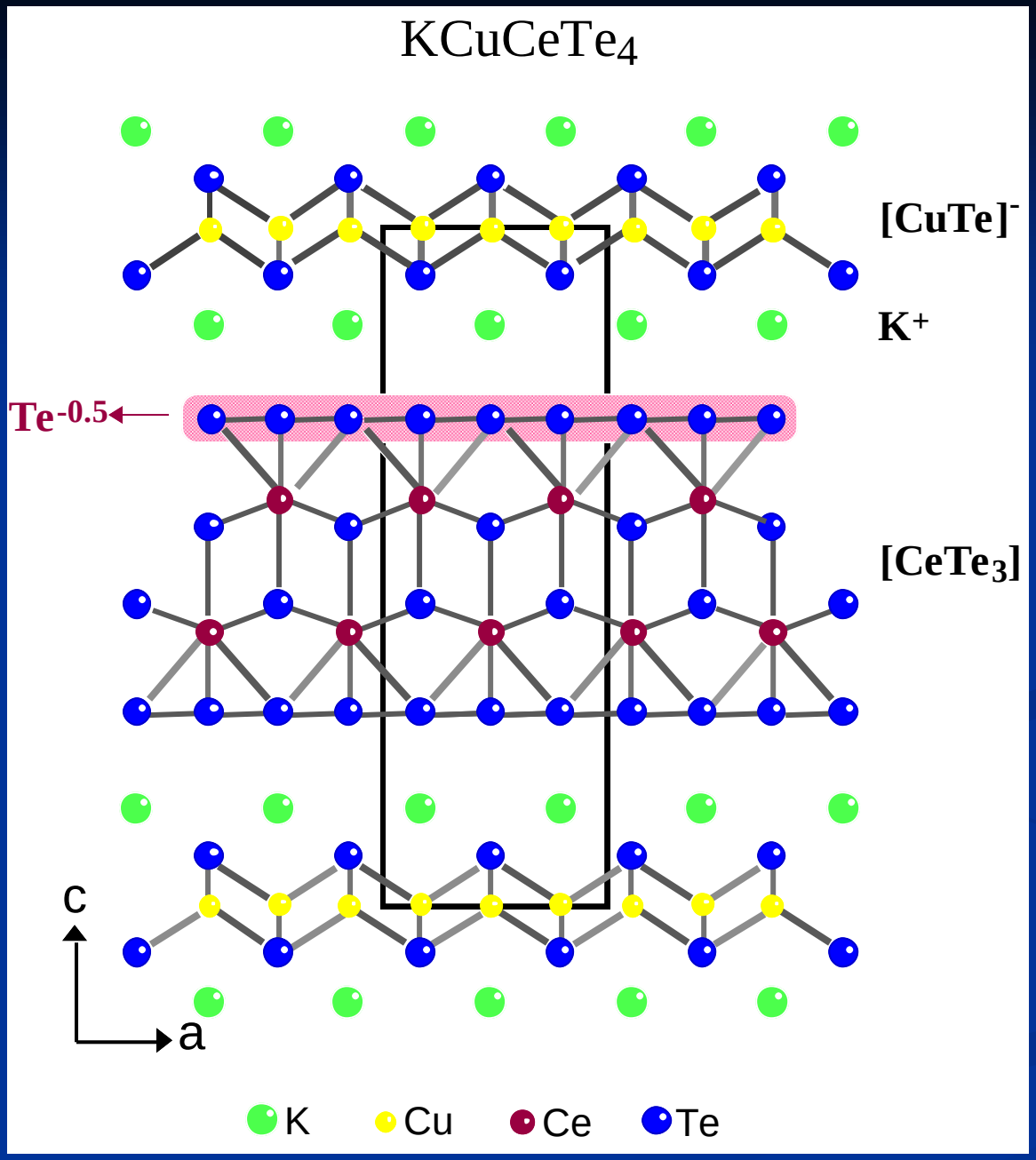
3 Te_3^{2-} or
1 Te_3^{2-}, 1 Te_5^{2-} and 1 Te^{2-}

O. Gourdon, J. Hanko, F. Boucher, V. Petricek, M.-H. Whangbo, M. G. Kanatzidis & M Evain, *Inorg. Chem.* 2000, 39, 1398

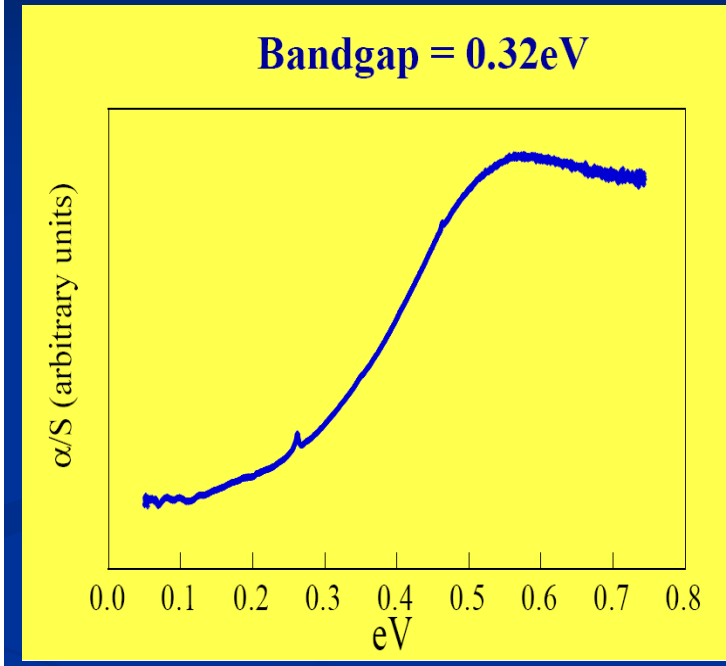
Distorted Net: band gap



$KCuCeTe_4$



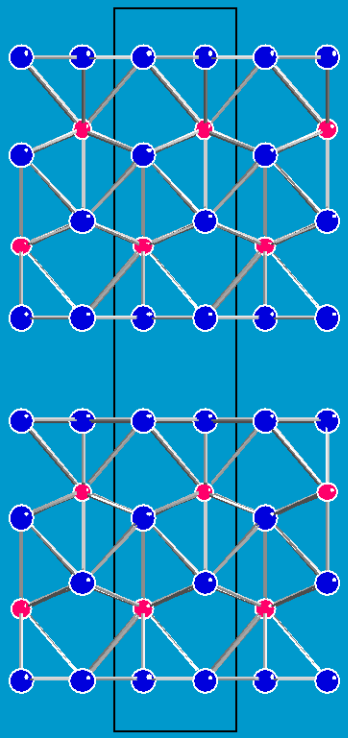
$KCuTe(CeTe_3)$



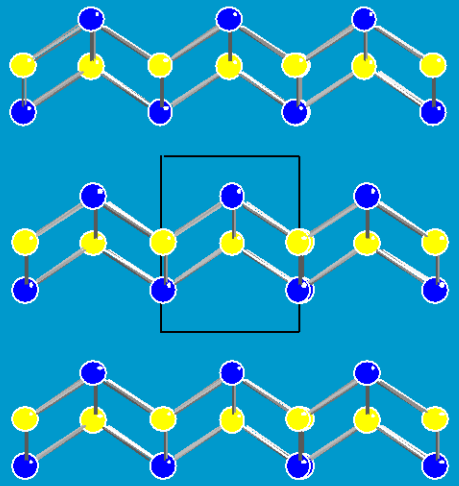
Patschke, Heising, Brazis, Kannewurf, and Kanatzidis, *Chem. Mater.* , **1998**, 10, 695

Thermodynamic Sinks

$$A_2Te + M_c + Ln + Te \xrightarrow{\text{phase separation}} LnTe_3 + M_cTe$$



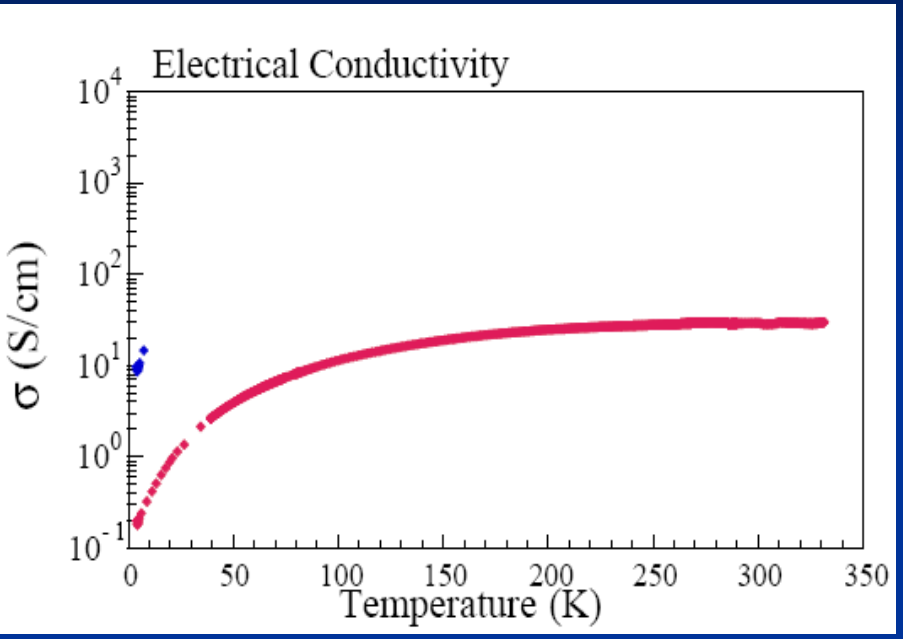
$NdTe_3$

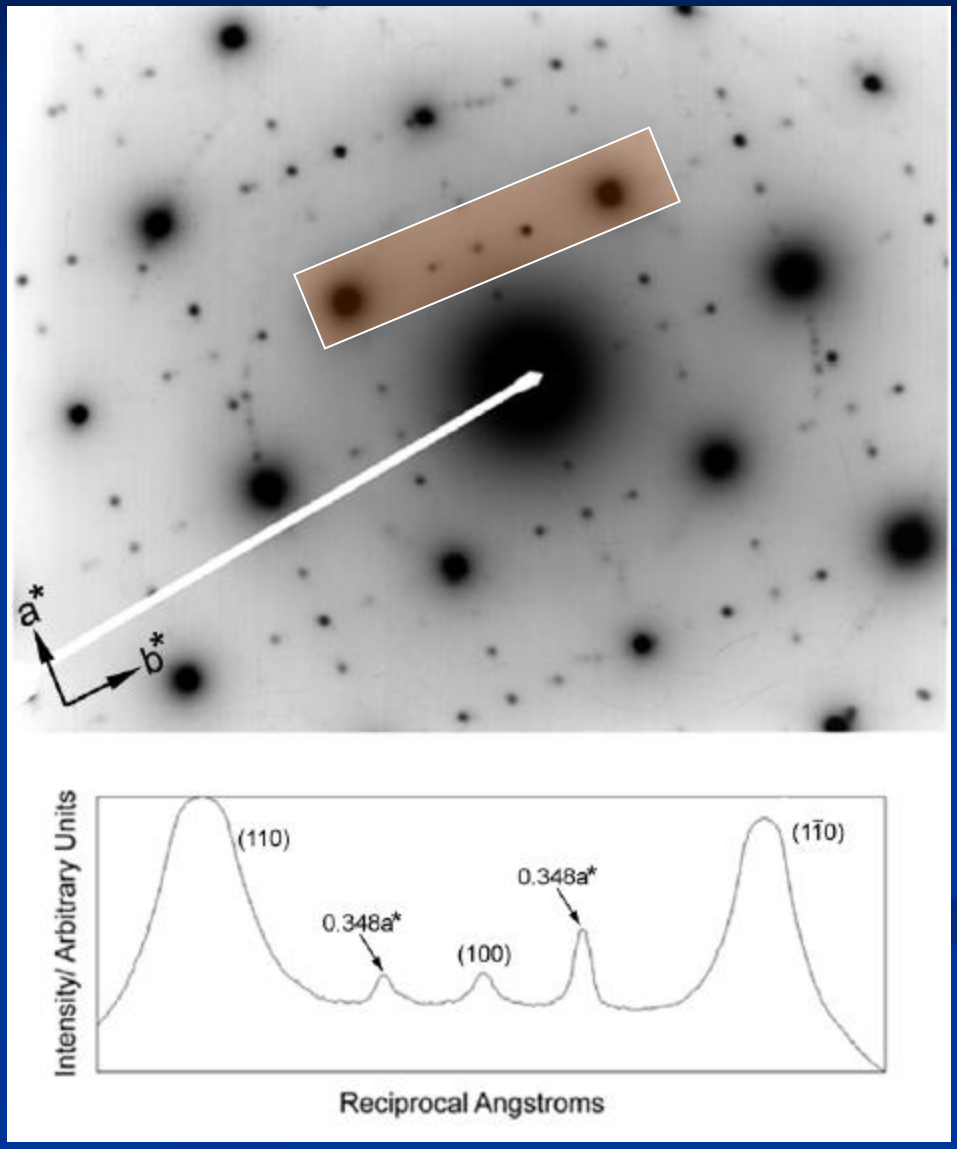


CuTe

NaCuTe

Electron Diffraction of $KCuCeTe_4$

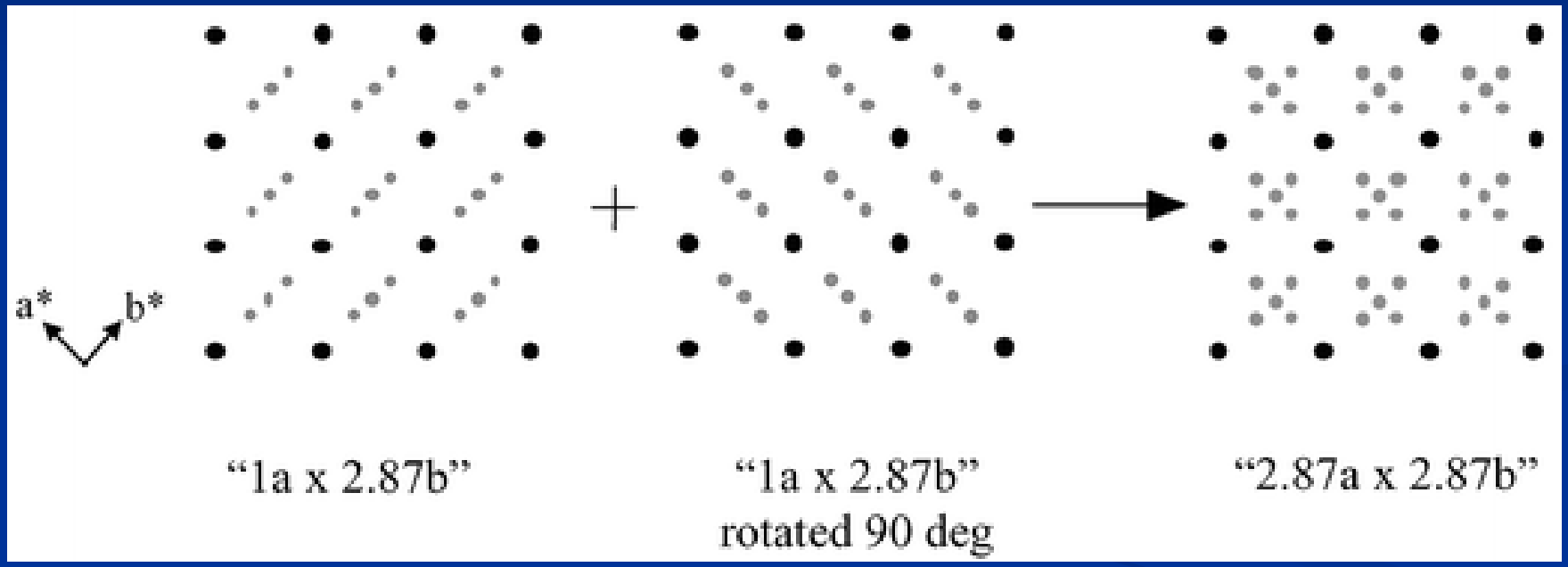




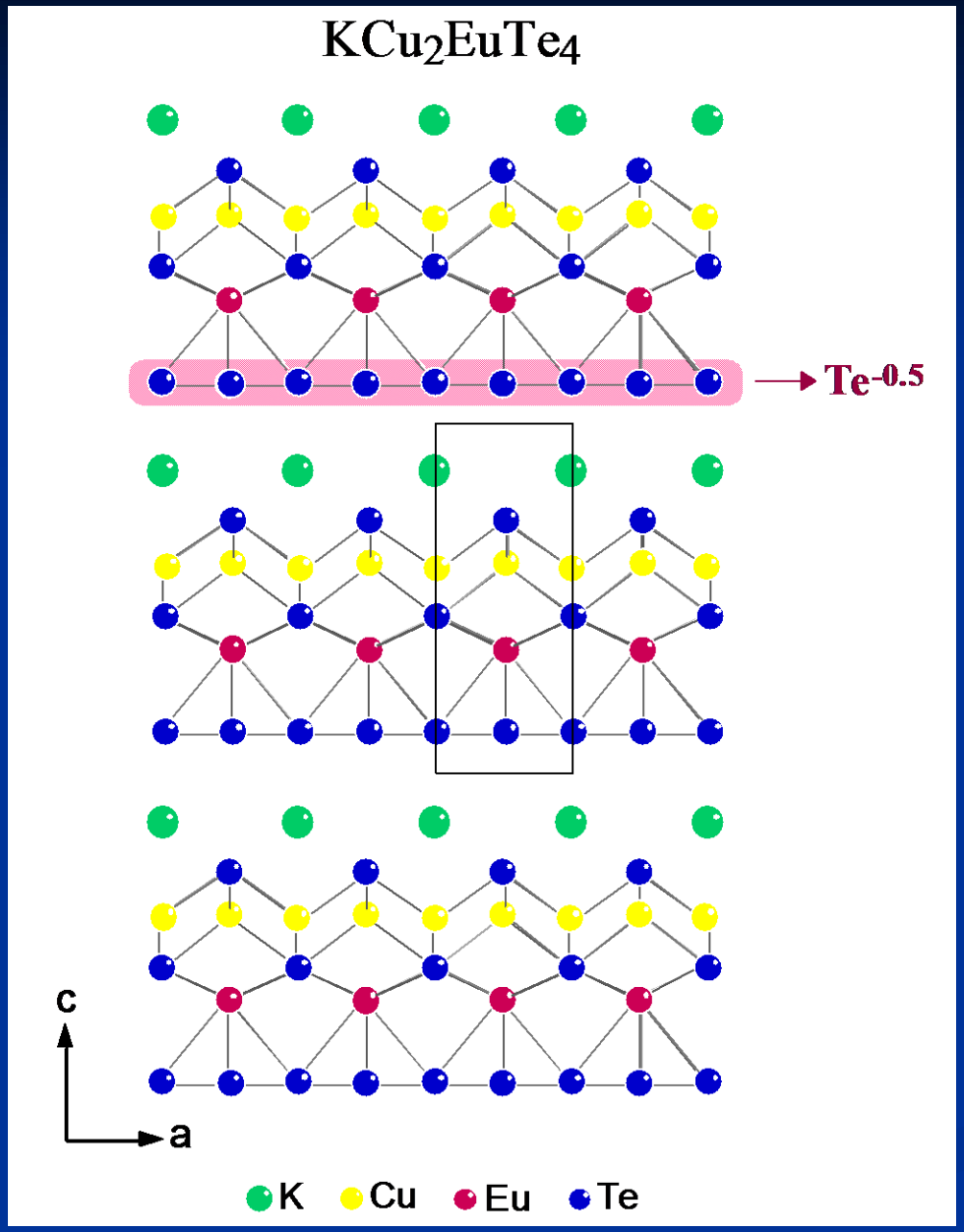
$KCuTe(CeTe_3)$

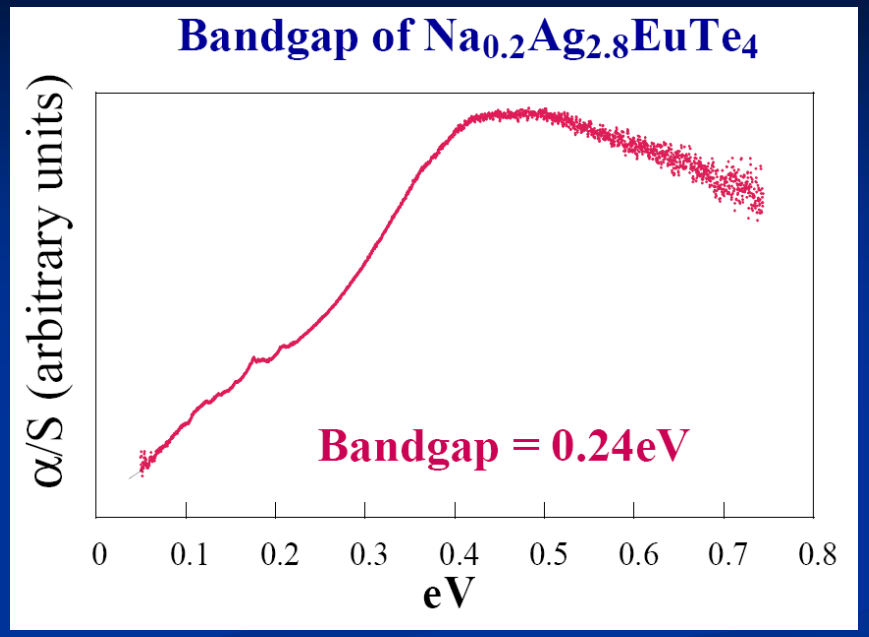
$(CeTe_3) = (CeTe)^+(Te_2)^-$

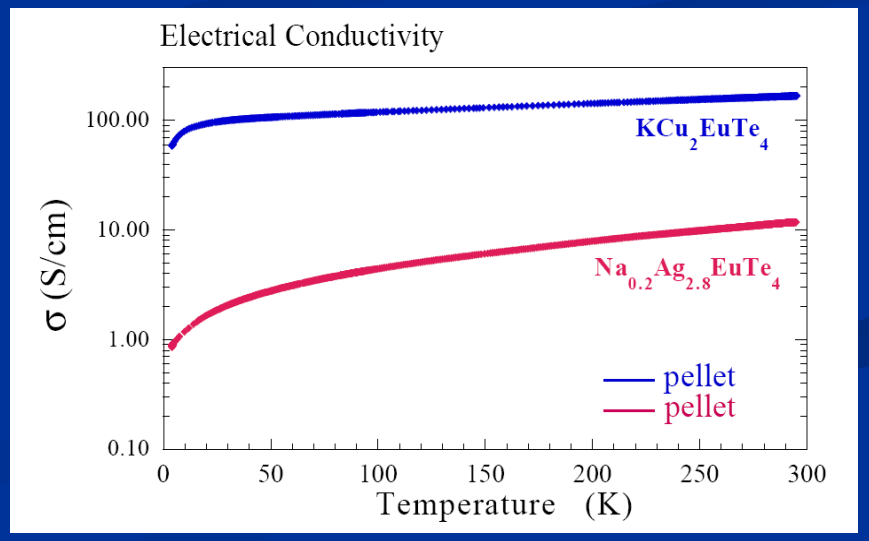
$(Te_2)^-$= tetramers Te_4^{2-} (or Te_2^{2-}/Te_6^{2-})


a*
b*
"1a x 2.87b"
"1a x 2.87b"
rotated 90 deg
"2.87a x 2.87b"

K^{+}, $2Cu^{1+}$, Eu^{2+}, $2Te^{2-}$, $2\ Te^{-0.5}$







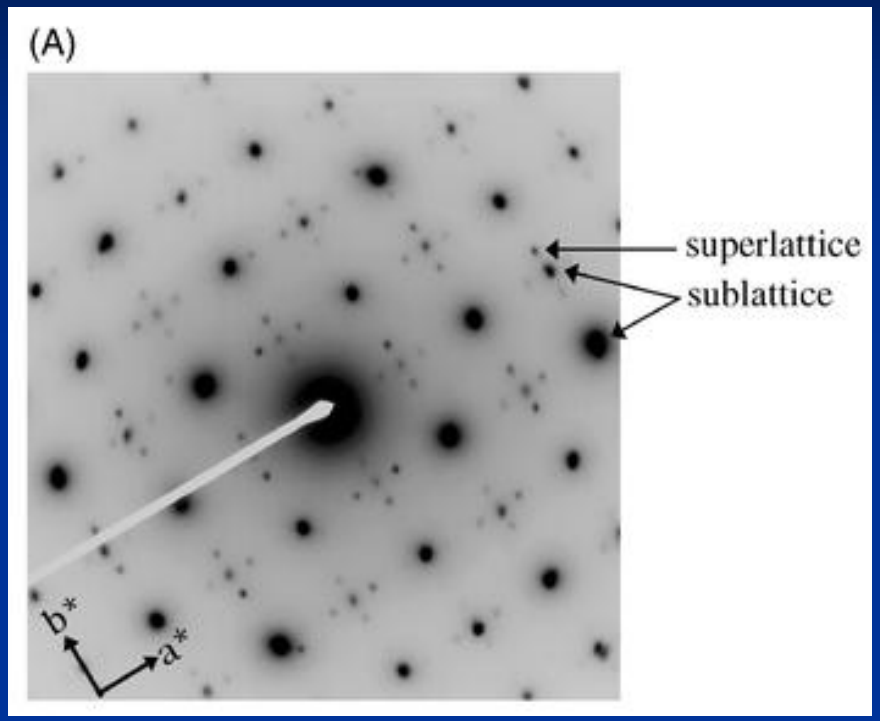
[AMEuTe] □divalent□ rare-earth meta

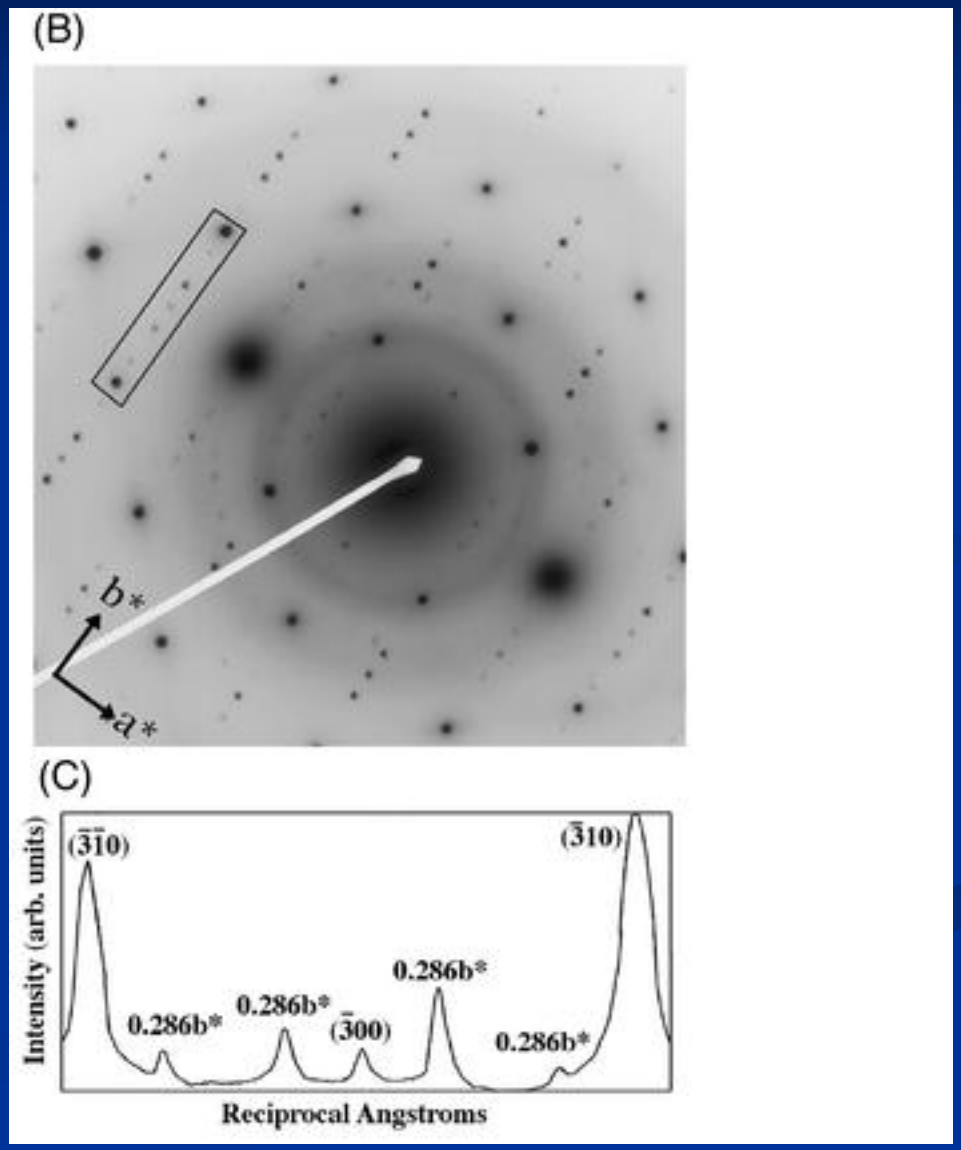
$$2K_2Te + 1Cu + 1Eu + 7Te \xrightarrow{850C/6d} KCu_2EuTe_4$$

$$4Na_2Te + 3Ag + 1Eu + 16Te \xrightarrow{850C/6d} Na_{0.2}Ag_{2.8}EuTe_4$$

Formula	KCu_2EuTe_4	$Na_{0.2}Ag_{2.8}EuTe_4$
Space Group	*P 4mm*	*P4mm*
a, □	4.4365(6)	4.4573(6)
c, □	11.365(2)	11.112(2)
V, □^{3}	223.69(6)	220.78(6)
Z	1	1
R/wR2	7.3/17.8	6.8/18.8
Goof	1.198	1.077

KCu_2EuTe_4 $^2/_7$ *a*- supercell





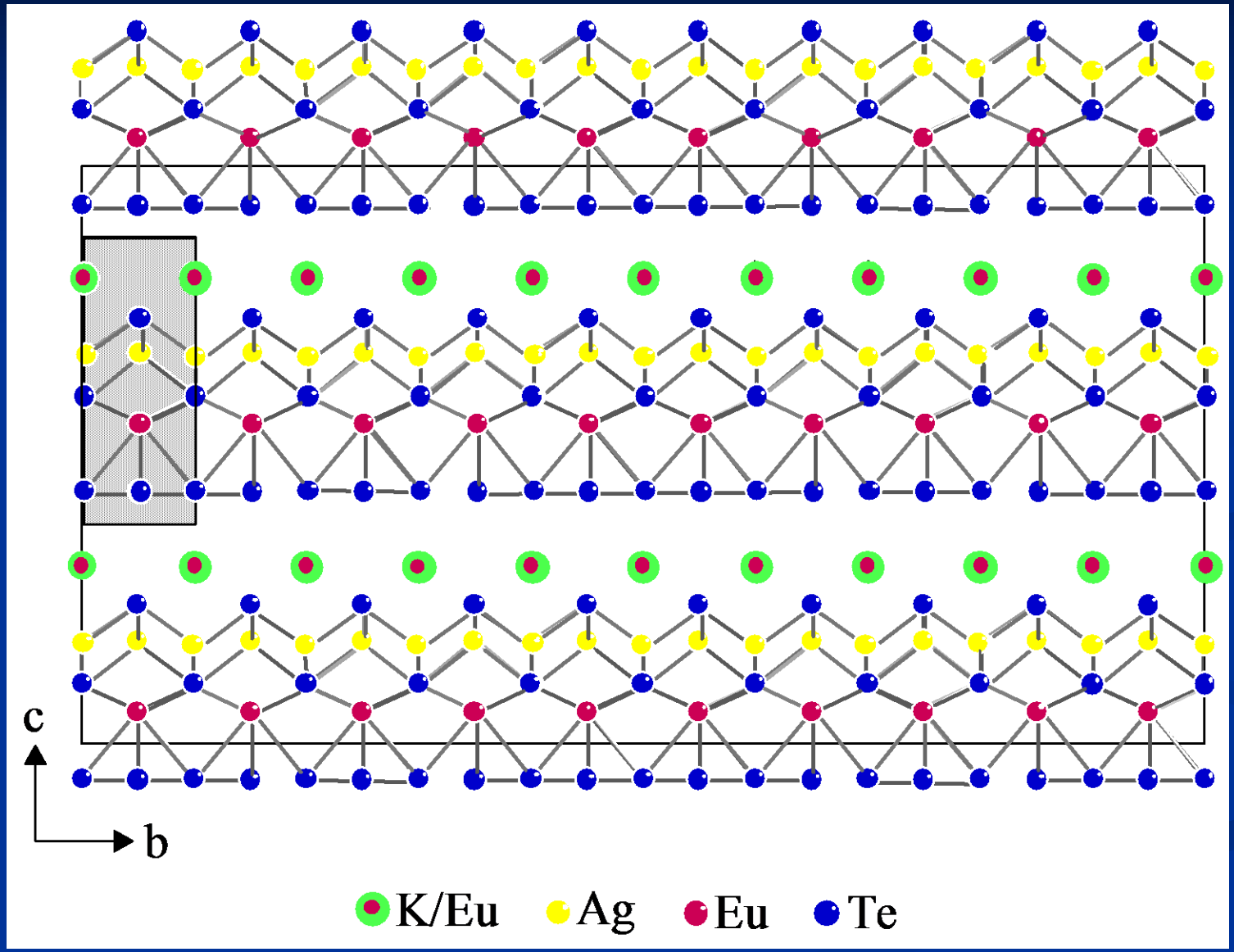
KCu_2EuTe_4: Elemental Substitution of □Cu□ with □Ag

$$2K_2Te + 1Ag + 1Eu + 8Te \xrightarrow{450C/3d} K_{0.65}Ag_2Eu_{1.35}Te_4$$

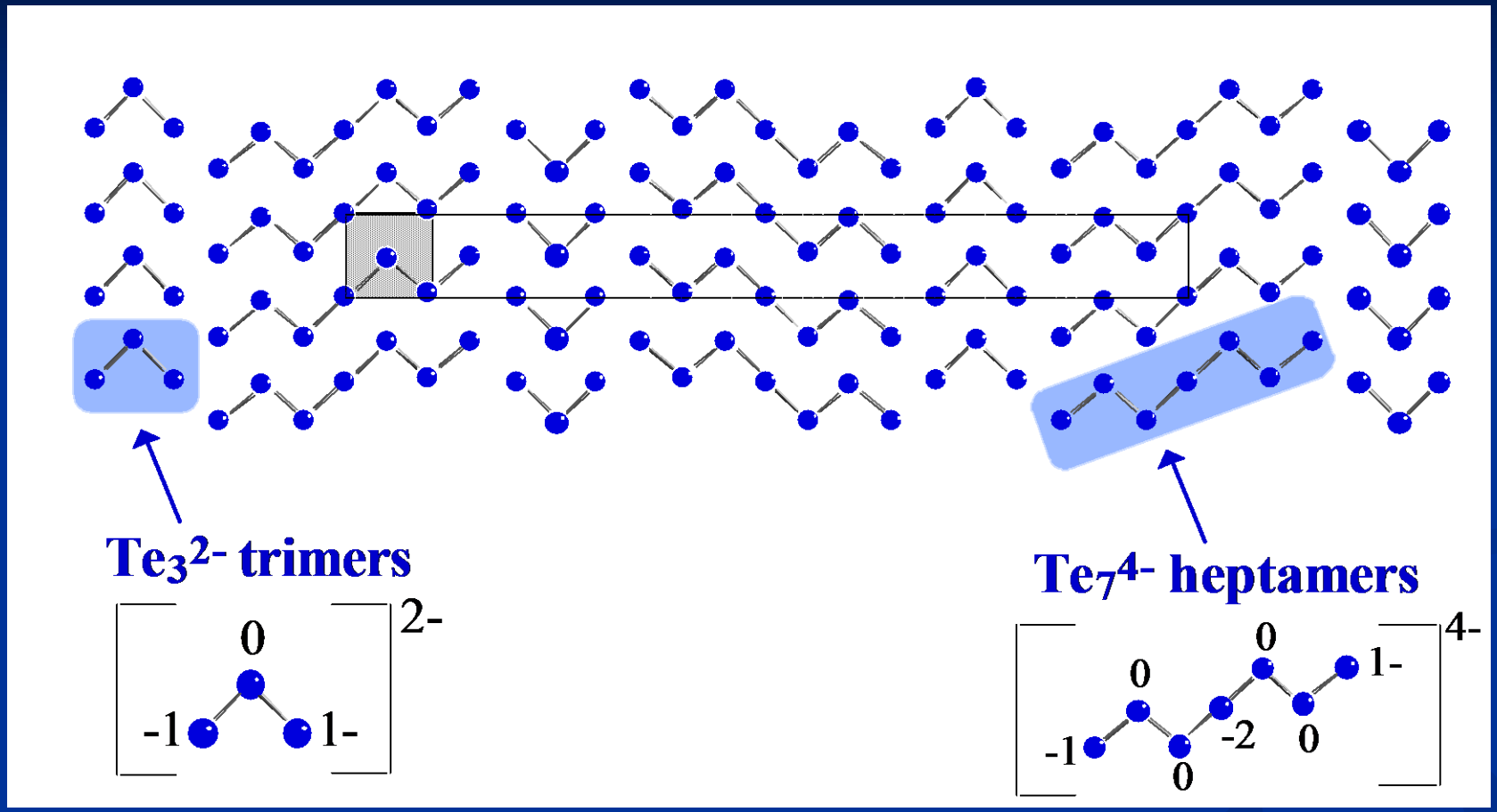
$$KCu_2EuTe_4 \xrightarrow{\text{-35\% K and +35\% Eu}} K_{0.65}Ag_2Eu_{1.35}Te_4$$

crystal data	KCu_2EuTe_4		$K_{0.65}Ag_2Eu_{1.35}Te_4$
Space group	P4mm		Abm2
a, Å	4.4365(6)	1a →	4.4989(9)
b, Å	4.4365(6)	10b →	45.279(9)
c, Å	11.365(2)	2c →	22.799(5)
V Å ^{3}	223.69(6)		4644(1)
Z	1		20
R1/wR2	7.3/17.8		6.46/27.80
	1a x 7b supercell		**1a x 10b x 2c supercell**

$K_{0.65}Ag_2Eu_{1.35}Te_4$ 1*a* x 10*b* x 2*c* supercell, *A bm2*

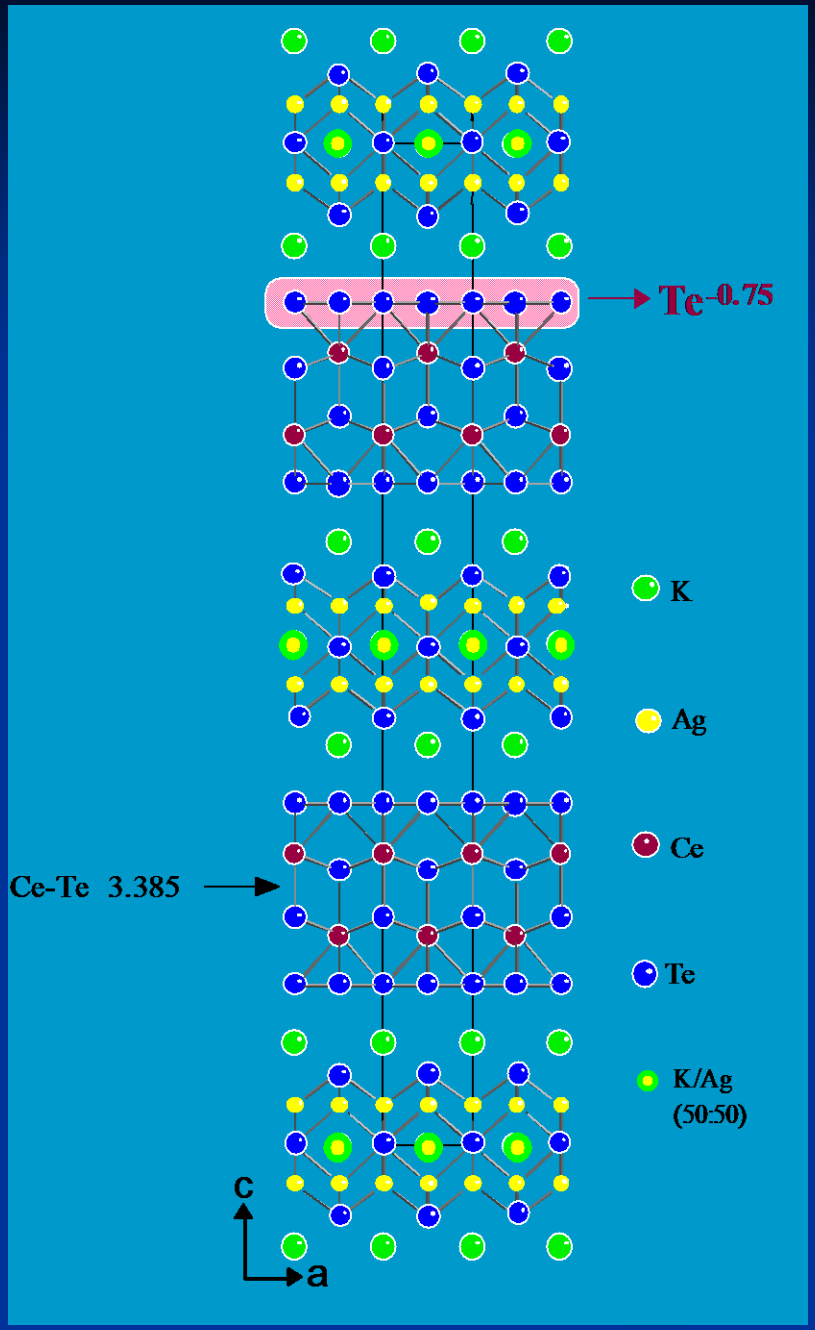


Distorted net in $K_{0.65}Ag_2Eu_{1.35}Te_4$

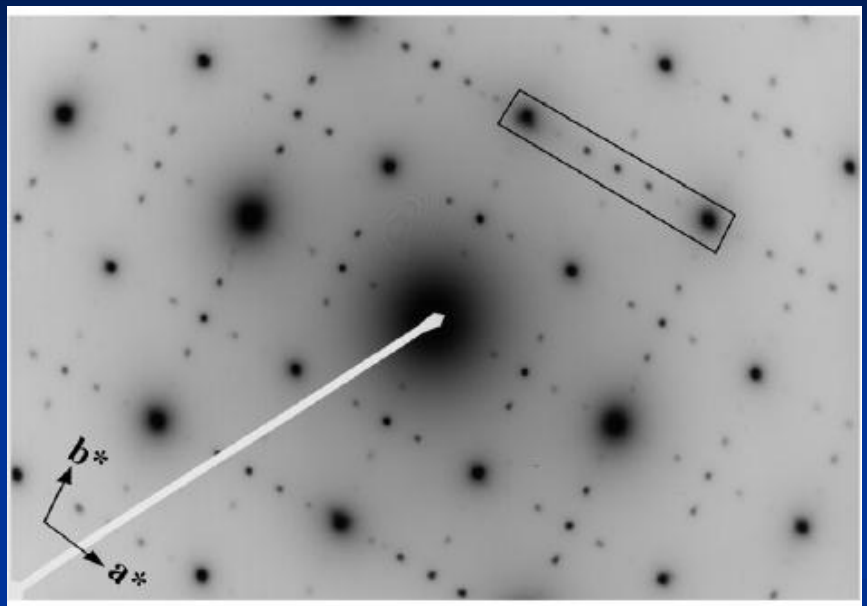


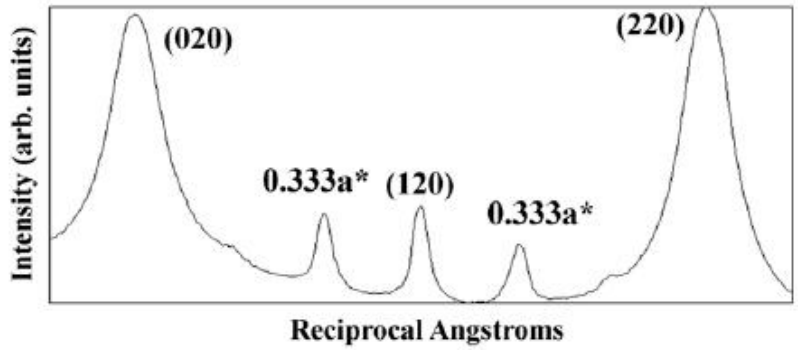
$Te^{-0.67}$ vs $Te^{-0.60}$

$K_{2.5}Ag_{4.5}Te_3(CeTe_3)_2$



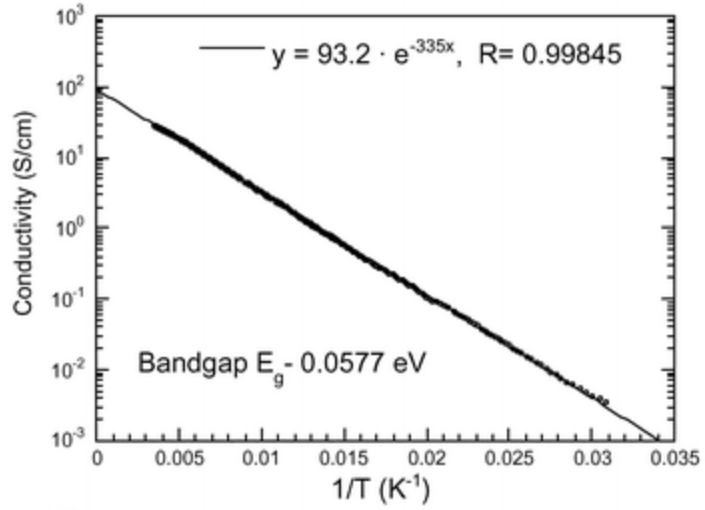
$K_{2.5}Ag_{4.5}Ce_2Te_9$

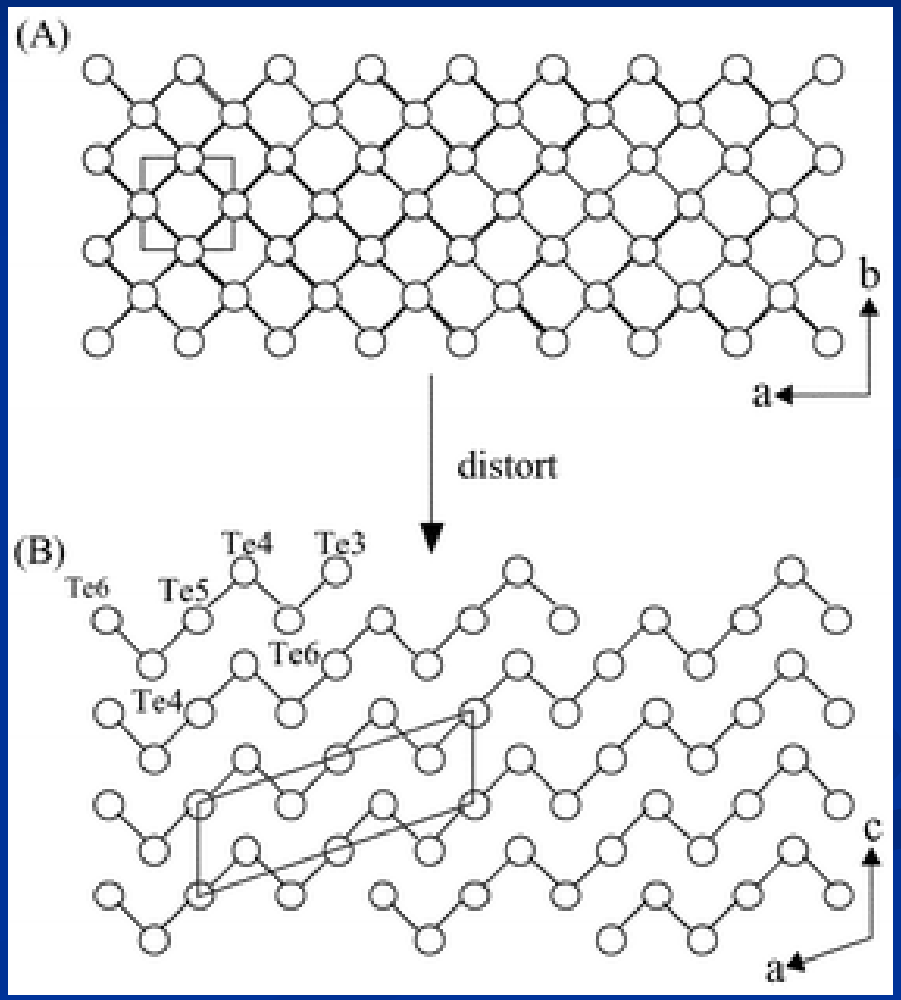




$K_{2.5}Ag_{4.5}La_2Te_9$ and $K_{2.5}Ag_{4.5}Ce_2Te_9$

Subcell	Supercell
$a = 4.4844(9)$ Å	$a' = 14.130(3)$ Å
$b = 4.5116(9)$ Å	$b' = 50.441(10)$ Å
$c = 50.859(10)$ Å	$c' = 4.4492(9)$ Å
$\alpha = 90°$	$\alpha = 90°$
$\beta = 90°$	$\beta = 108.37(3)°$
$\gamma = 90°$	$\gamma = 90°$
$I\,mmm$	$C\,2/m$

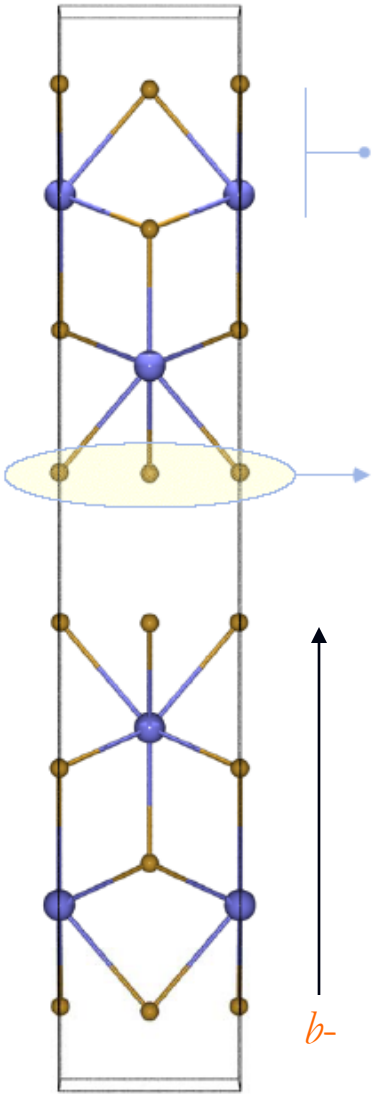




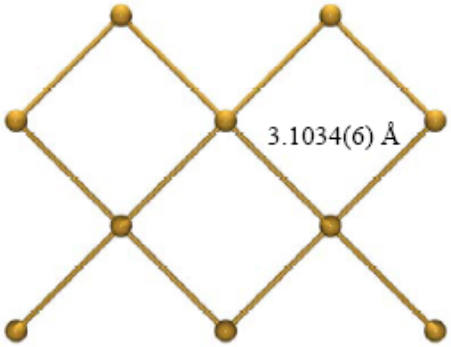
What about $RETe_3$?

- $RETe_3$ adopt the $NdTe_3$ structure type (*C mcm*)
  - $(NdTe)^{+}(Te^{-0.5})_2$
- Square Te nets
- TEM studies on $SmTe_3$ showed 3.5-fold superstructures: proposed trimers Te_3^{2-}
  - E. DiMasi, M. C. Aronson, J. F. Mansfield, B. Foran and S. Lee, *Phys. Rev.*, 1995, **B52**, 404.
  - B. Foran and S. Lee, *J. Am. Chem. Soc.*, 1994, **116**, 154
- $LaTe_2$
  - $(LaTe)^{+}(Te^{-1})$ (superstructure has Te_2^{2-} dimers)
- $DySe_{1.84}$ was shown to posses a 66-fold superstructure (Lee et al)

Average Structure of $CeTe_3$



The average structure consists of puckered double layers of rare earth and tellurium that are separated by two "square" planar nets of tellurium. The average charge per Te atom in the net is -0.5e



Crystal Data

Orthorhombic Cmcm (#63)

a = 4.3800(12) Å

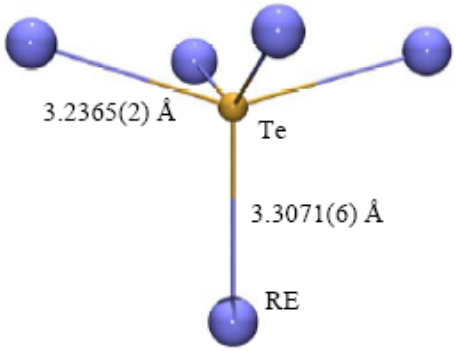
b = 26.056(7) Å

c = 4.3976(12) Å

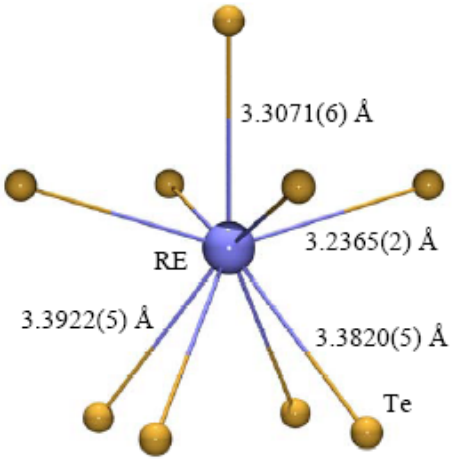
R_1/wR_2 [I>2σ(I)] = 1.64/4.22

$CeTe_3$

b-

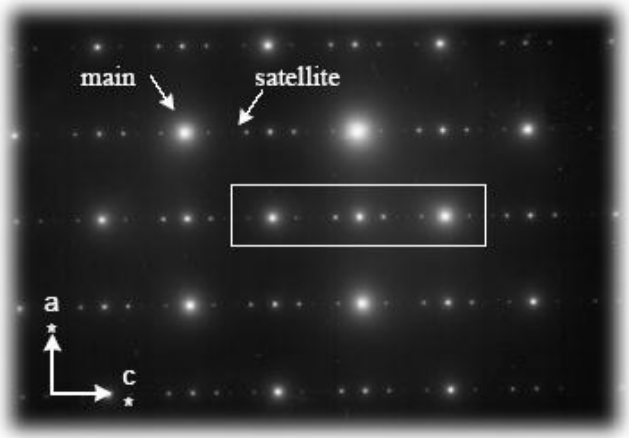


The tellurium atom is coordinated by five rare earth atoms in a square-pyramidal way

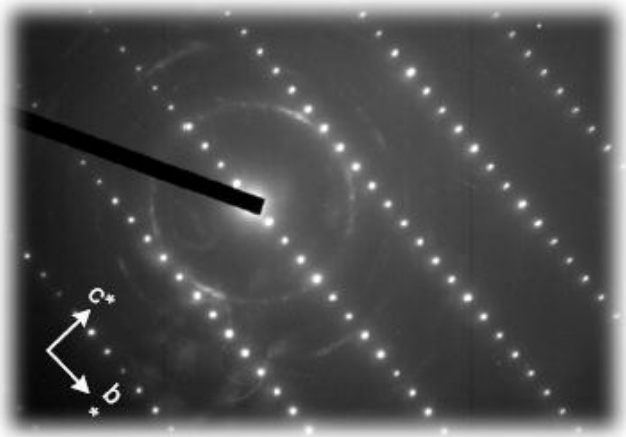


The rare earth is surrounded by nine tellurium atoms forming a monocapped tetragonal antiprism

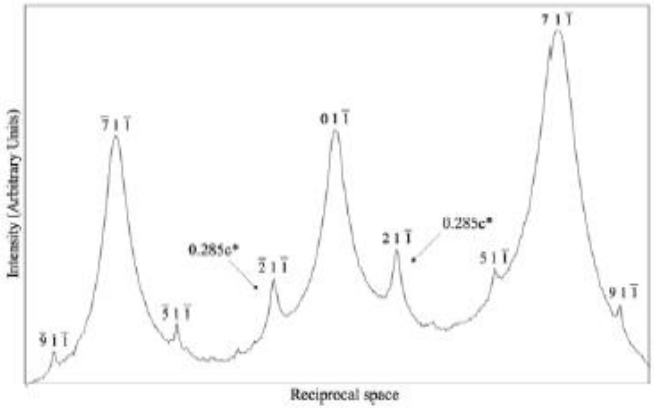
Transmission Electron Microscopy (TEM) study



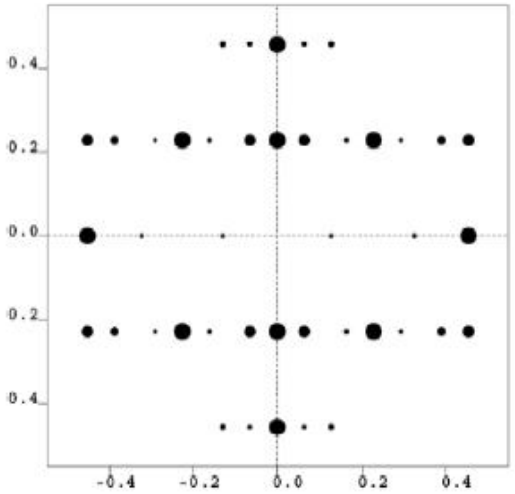
Selected area electron diffraction pattern of $CeTe_3$ at the $[010]_t$ orientation showing the $7c_{sub}$ superlattice



Selected area electron diffraction pattern of $CeTe_3$ at the $[100]_t$ orientation (cross section). There is no modulation along the b* direction since there are no supplementary supercell spots



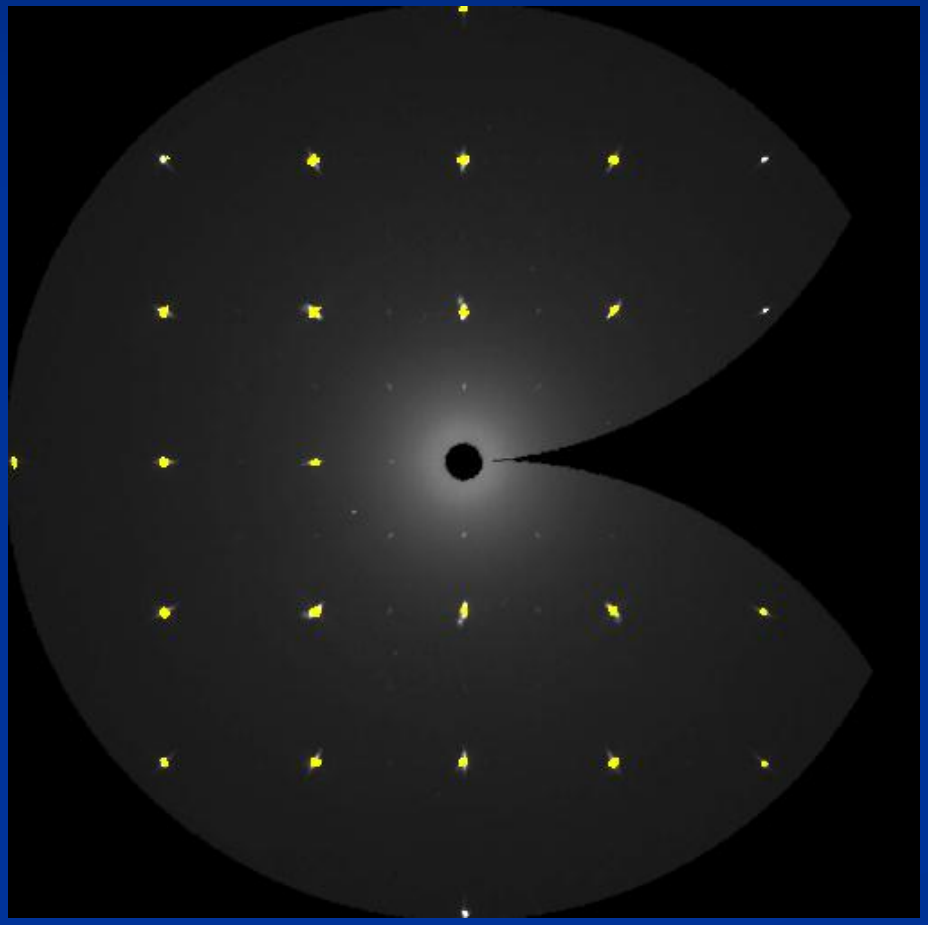
Intensity scan along the (h1-1) row of reflections shows the satellite reflections located at a distance of 0.285c* from the main (01-1) spot. This distance corresponds to a q-vector of 2/7

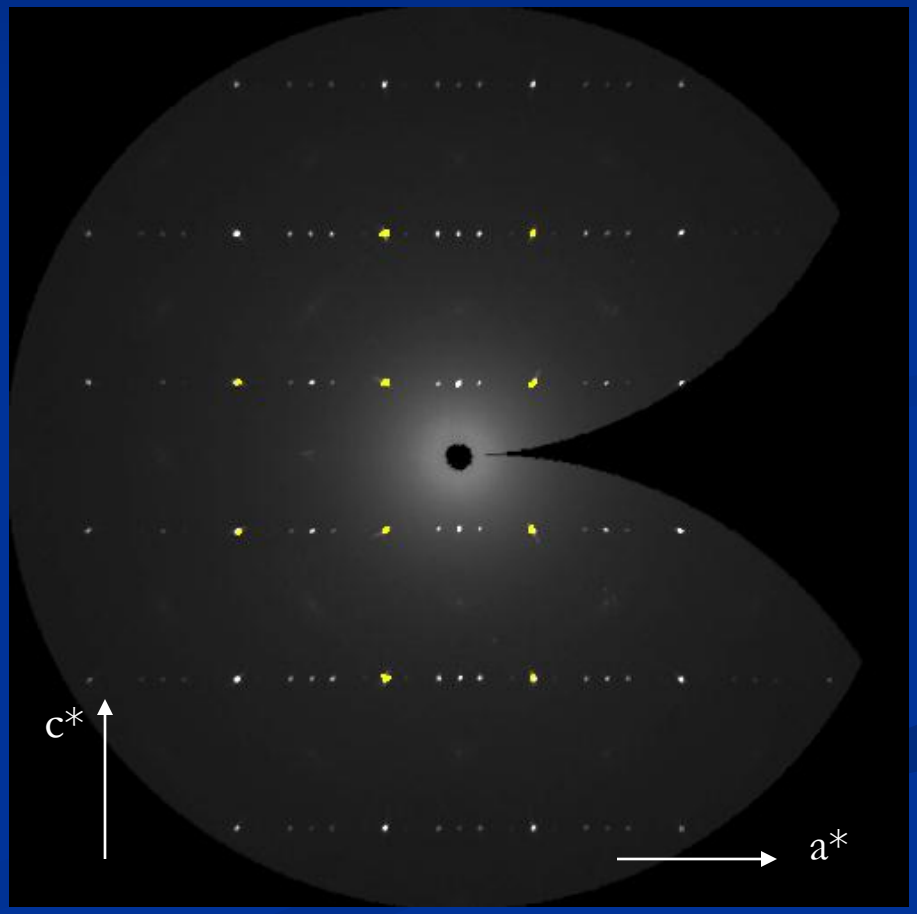


Calculated diffraction pattern from the supercell. The zone axis is [0 1 0] and the specimen thickness 20 Å

Single Crystal Diffraction Analysis

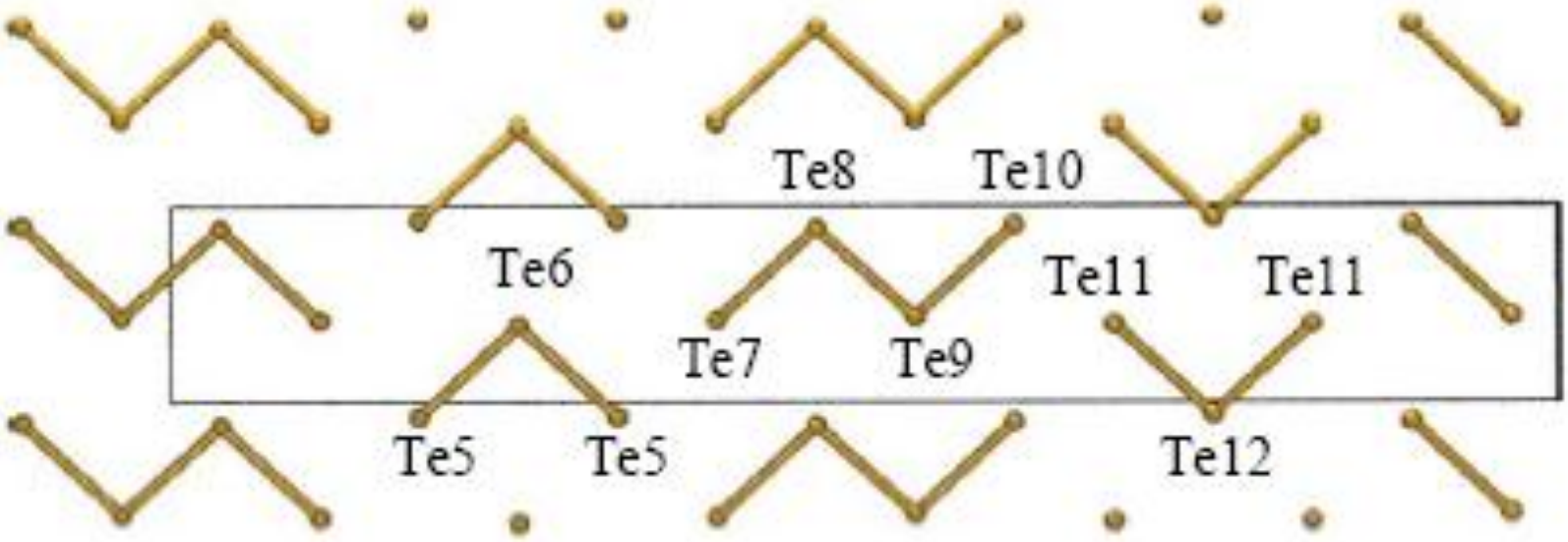
Precession photos





Resolving the Distortion in $RETe_3$: trimers and tetramers

Te_3^{2-}
Te_4^{2-}

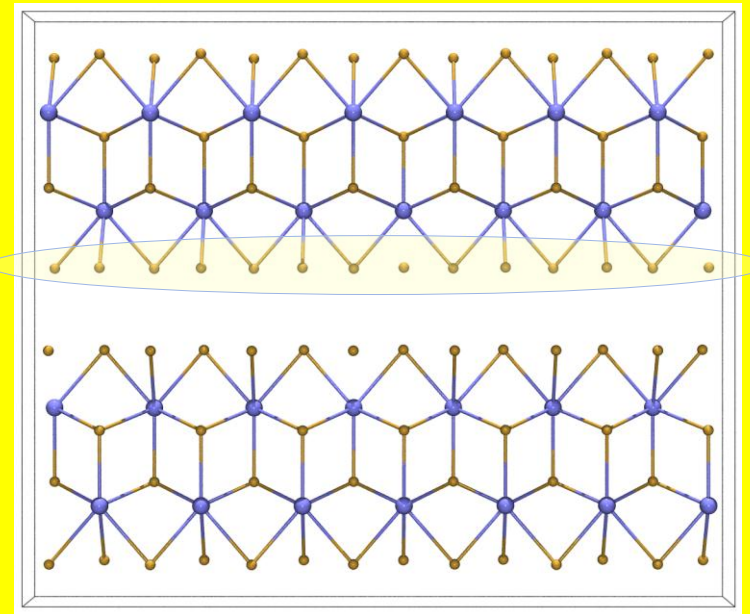


Crystal Data

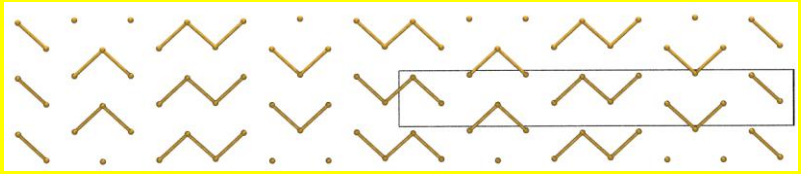
$CeTe_3$	$PrTe_3$	$NdTe_3$	$SmTe_3$	$GdTe_3$
Ama2 (#40)	Ama2 (#40)	Ama2 (#40)	Ama2 (#40)	Ama2 (#40)
a = 30.800(8) Å	a = 30.640(8) Å	a = 30.561(6) Å	a = 30.383(8) Å	a = 30.307(7) Å
b = 26.055(7) Å	b = 25.915(7) Å	b = 25.859(5) Å	b = 25.676(6) Å	b = 25.573(6) Å
c = 4.3810(12) Å	c = 4.3598(11) Å	c = 4.3563(9) Å	c = 4.3341(11) Å	c = 4.3162(9) Å
R_1/wR_2 = 3.82/8.83	R_1/wR_2 = 4.98/14.69	R_1/wR_2 = 4.81/12.43	R_1/wR_2 = 5.30/20.28	R1wR2 = 5.44/10.54

Resolving the Distortion in $RETe_3$

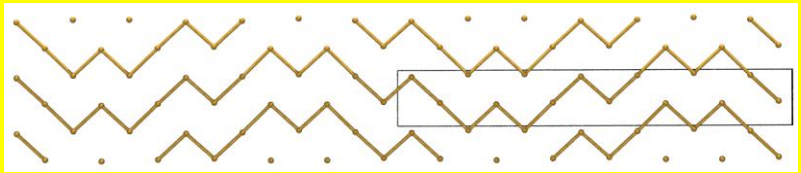
Te_3^{2-}
Te_4^{2-}



The supercell has a $c=7c_{sub}$ axis. The modulation is mostly located in the Te net which results a wide distribution of distances between the atoms.
For $CeTe_3$ the minimum distance is 2.94(2) Å and the maximum 3.26(3) Å with an average of 3.11(3) Å



Bonding cutoff less than 3.020 Å the net reveals V-shaped trimers and N-shaped tetramers.



With bonding cutoff of 3.100 Å

Crystal Data

$CeTe_3$	$PrTe_3$	$NdTe_3$	$SmTe_3$	$GdTe_3$
Ama2 (#40)	Ama2 (#40)	Ama2 (#40)	Ama2 (#40)	Ama2 (#40)
a = 30.800(8) Å	a = 30.640(8) Å	a = 30.561(6) Å	a = 30.383(8) Å	a = 30.307(7) Å
b = 26.055(7) Å	b = 25.915(7) Å	b = 25.859(5) Å	b = 25.676(6) Å	b = 25.573(6) Å
c = 4.3810(12) Å	c = 4.3598(11) Å	c = 4.3563(9) Å	c = 4.3341(11) Å	c = 4.3162(9) Å
R_1/wR_2 = 3.82/8.83	R_1/wR_2 = 4.98/14.69	R_1/wR_2 = 4.81/12.43	R_1/wR_2 = 5.30/20.28	R1wR2 = 5.44/10.54

4D structure refinement based on q-vector

Crystal Data

C2cm(00g)000 (#40.1)

a = 4.3466(10) Å

b = 25.8330(50) Å

c = 4.3644(8) Å

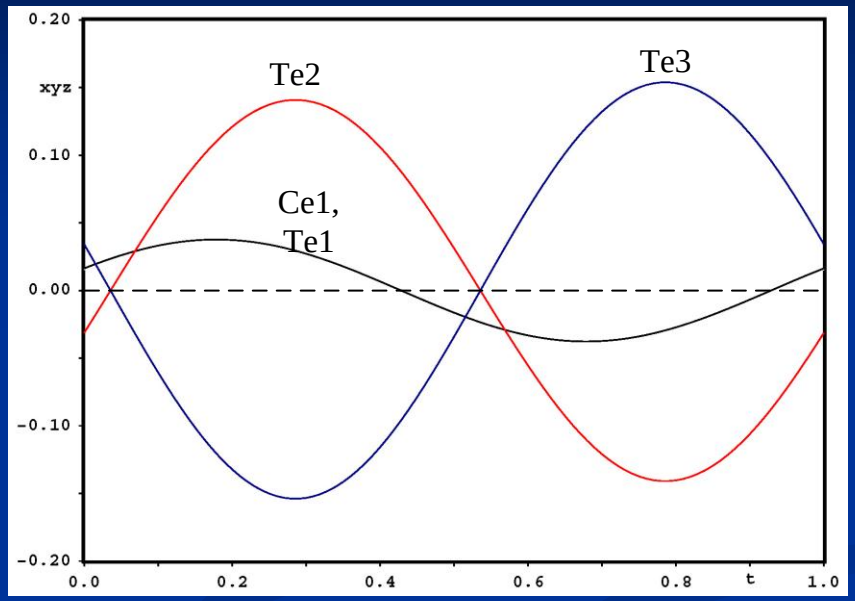
q = 0.282c* (2/7c*)

R_1/wR_2 (all) = 2.57/7.93

R_1/wR_2 (main) = 1.66/6.53

R_1/wR_2 (satellites) = 7.47/11.31

$NdTe_3$



direction (t). The line at zero represents the initial position of the atoms in the subcell.

Tellurium atoms in the net (Te2 and Te3) have the largest displacement.

For the $CeTe_3$ the minimum distance is 2.861(3) Å and the maximum 3.279(4) Å with an average

JANA 2000
V. Petricek

7-fold superstructure puzzling

- Superstructure shows 2 Te_3^{2-} and 2 Te_4^{2-} i.e. $(Te_{14})^{8-}$
- $CeTe_3$ = $(CeTe)Te_2$ = 7-fold → $(CeTe)_7(Te_2)_7$
- (CeTe)+ therefore $(Te_{14})^{7-}$
- $(Te_{14})^{8-}$ vs $(Te_{14})^{7-}$?
- Explains close distances between Te_3^{2-} and Te_4^{2-}.

Are distortions characteristic of the bulk?

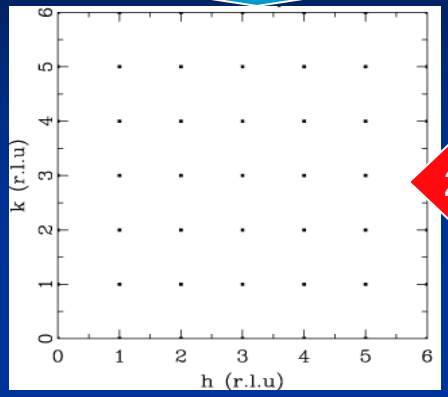
- Simple powder diffraction inadequate to detect superstructure
- PDF: a total scattering technique

Diffraction patterns from materials with different degrees of structural coherence

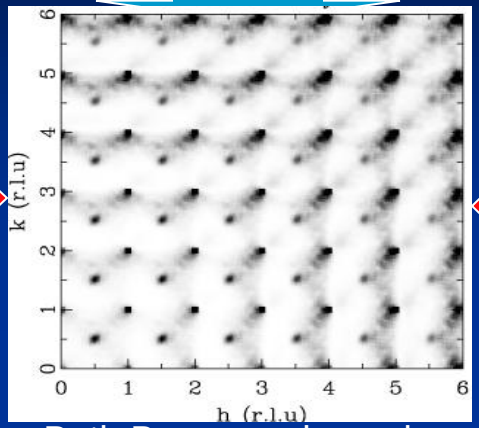
No disorder — Ideal (perfect) crystals

Moderate disorder — Real (imperfect) crystals

A great deal of disorder — Glass

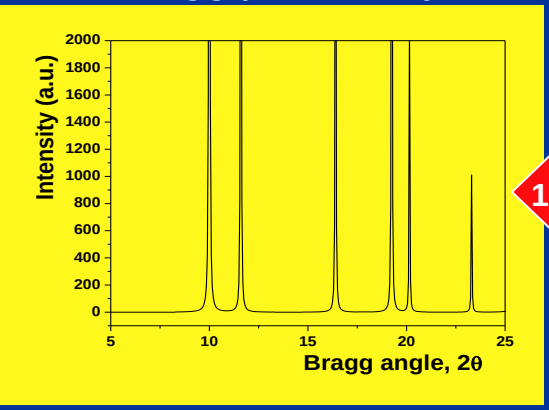


Simulated 2d patterns



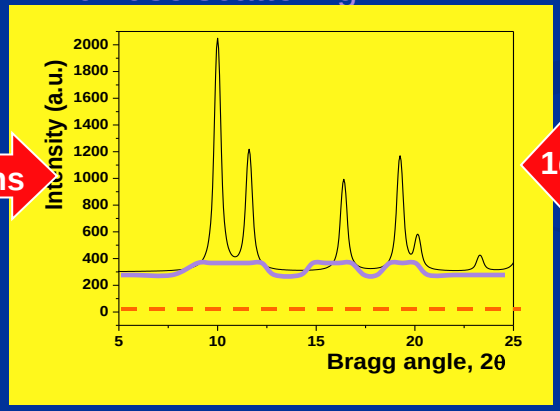
Simulated 2d patterns

Bragg peaks only



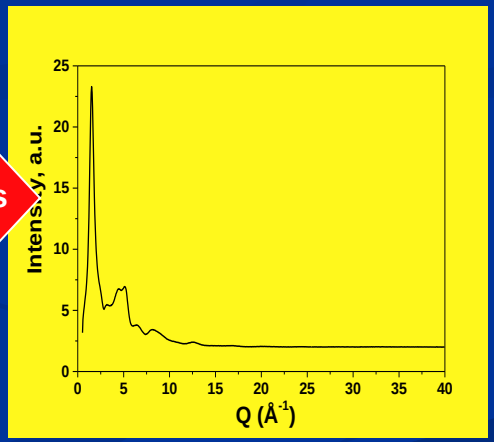
1d patterns

Both Bragg peaks and diffuse scattering



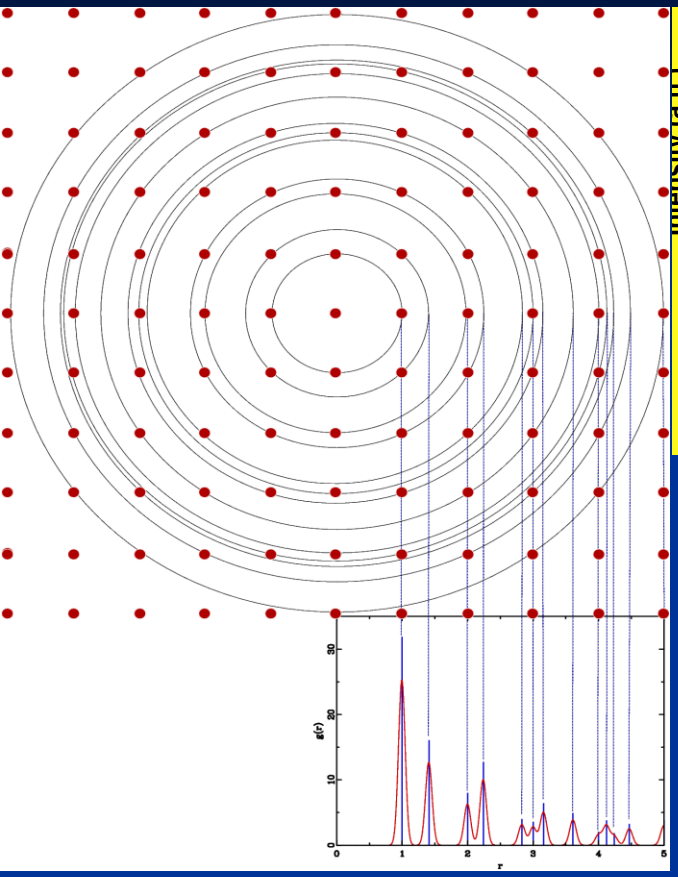
1d patterns

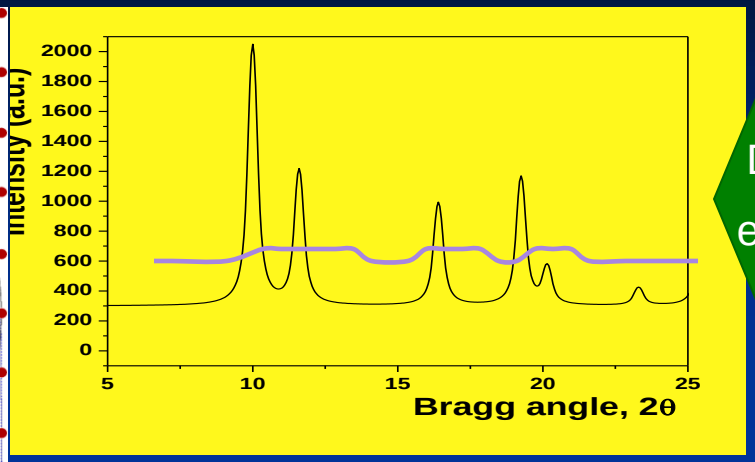
Diffuse scattering only



Diffraction patterns of perfect crystals show Bragg peaks only. Diffraction patterns of materials of limited structural coherence contain a diffuse component which is of low intensity and is widely spread in reciprocal space. All components of the diffraction patterns have to be accounted for to completely determine the atomic structure.

The Atomic Pair Distribution Function Technique





Diffraction experiment

$$S(Q) = 1 + \left[I^{el.}(Q) - \sum c_i f_i^2(Q) \right] / \left[\sum c_i f_i(Q) \right]^2$$

$$G(r) = (2/\pi) \int_{Q=o}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ,$$

$G(r) = 4\pi r[\rho(r) - \rho_o]$
$\rho(r)$ is the local and
ρ_o the average atomic density

G(r) ~ 1D Patterson function

$Q = 4\pi \sin(\theta)/\lambda = 1.0135 \sin(\theta) E[keV]$

Billinge, Egami

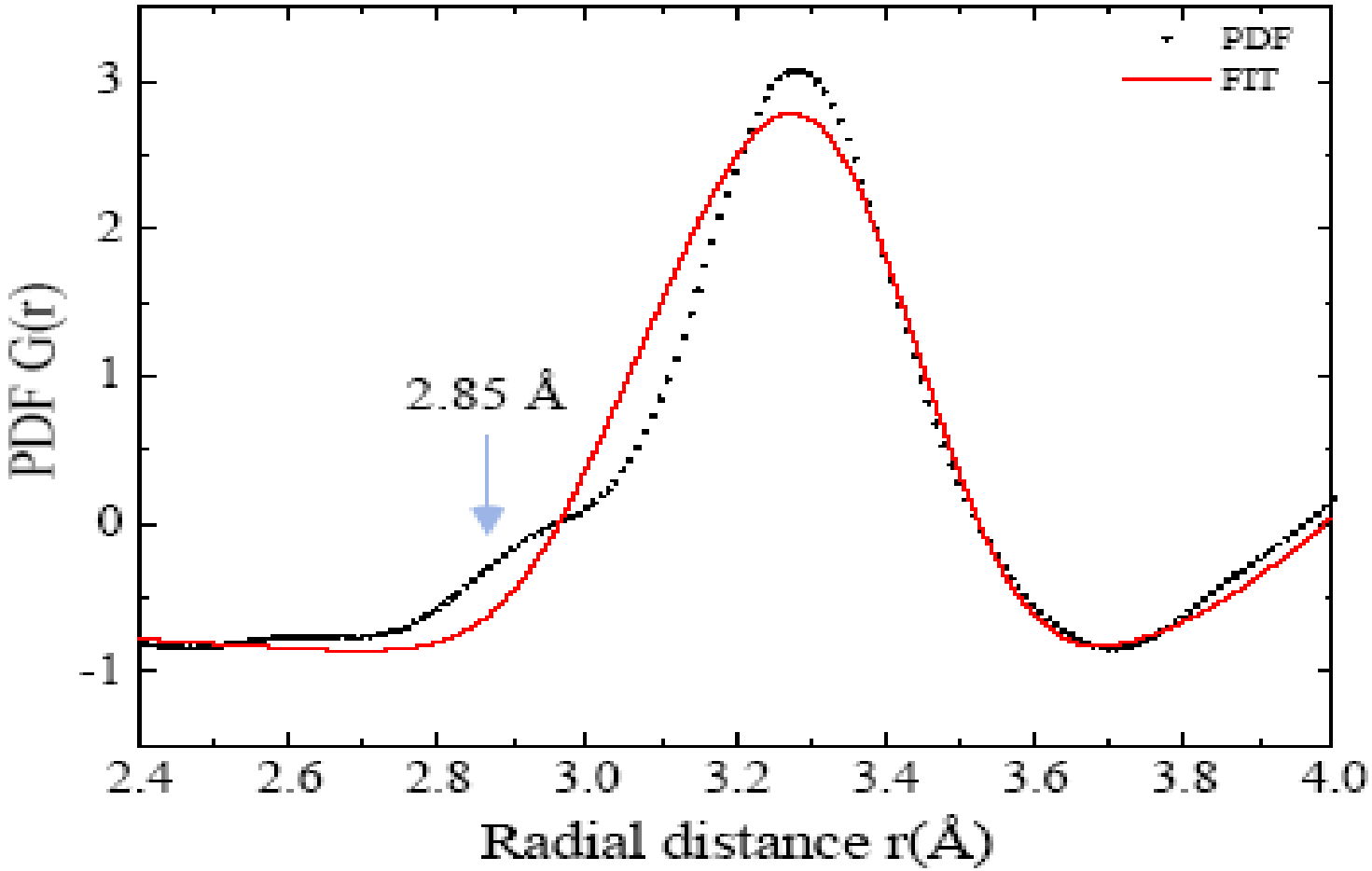
Properties of PDF, G(r)

- The atomic PDF, G(r), peaks at characteristic interatomic distances and thus reflects the structure of materials.
- It is the Fourier sine transform of the experimentally observable structure factor S(Q) which is related to the elastic part of the **total diffracted intensity**.
- Since both the sharp **Bragg peaks** and the diffuse components of the diffraction spectrum contribute to G(r) it reflects **both the average, long-range structure and the local structural imperfections.**
- High-resolution G(r)'s is obtained by accessing high values of Q. This can be done by using high energy x-rays.

Billinge, Egami

$CeTe_3$

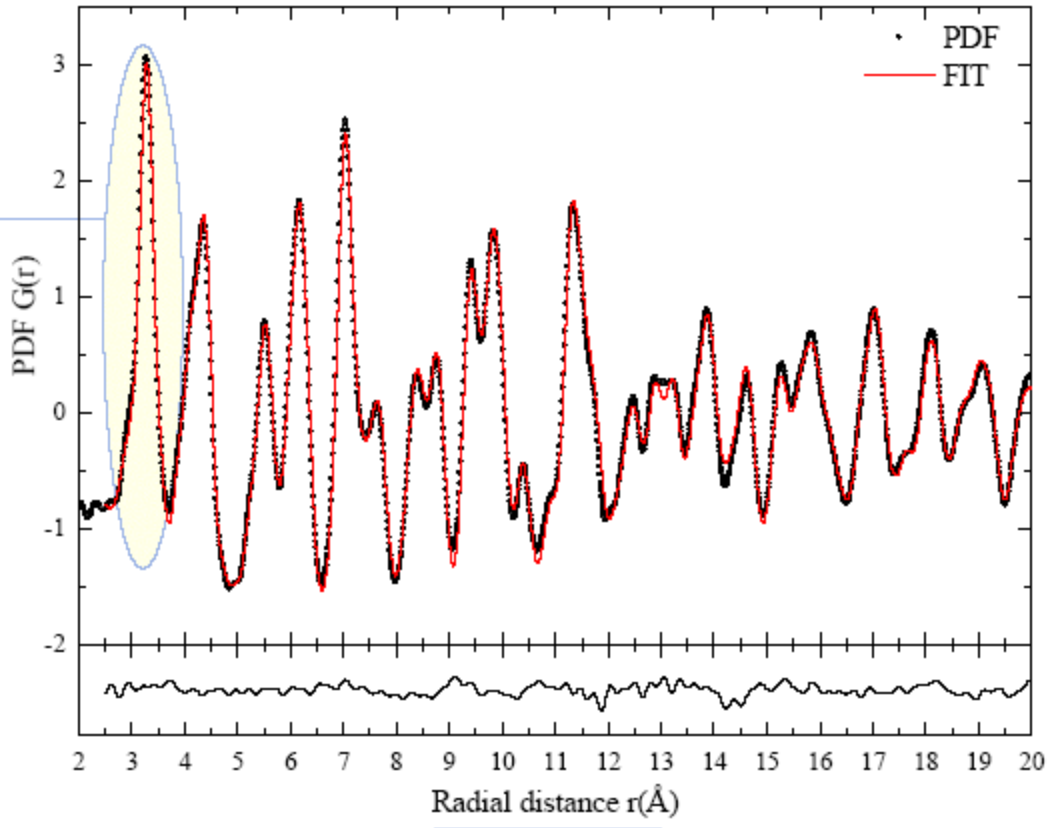
Total scattering and PDF for $CeTe_3$

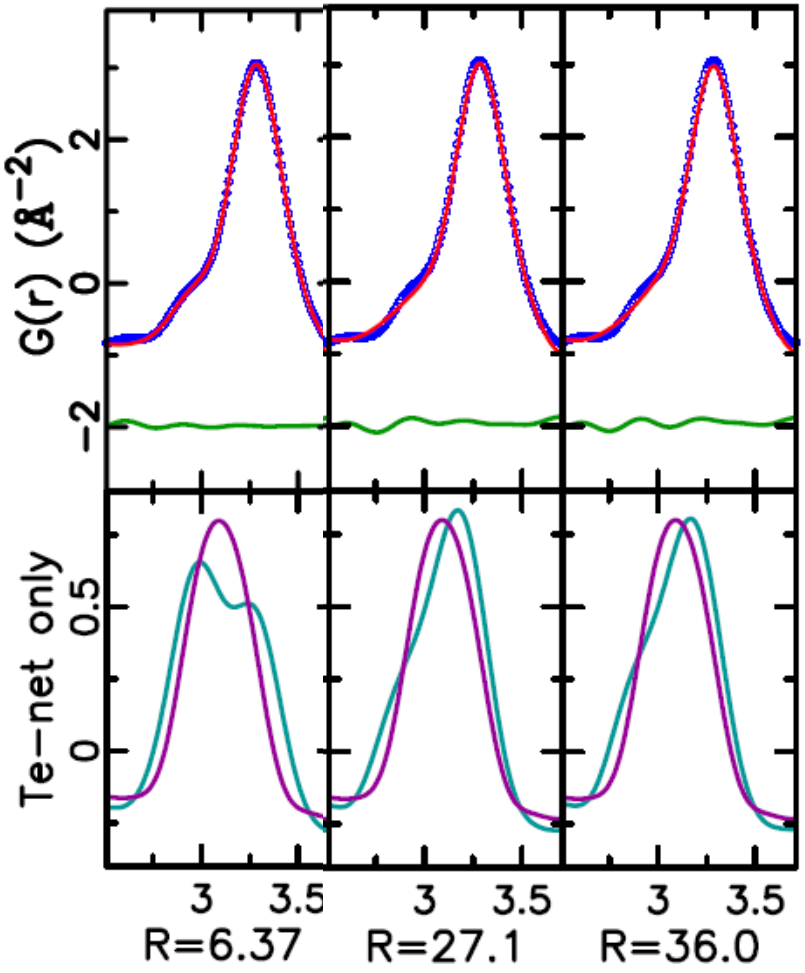


Fitting of the average structure. Due to the modulation there is a shoulder at the first peak around 2.85 Å

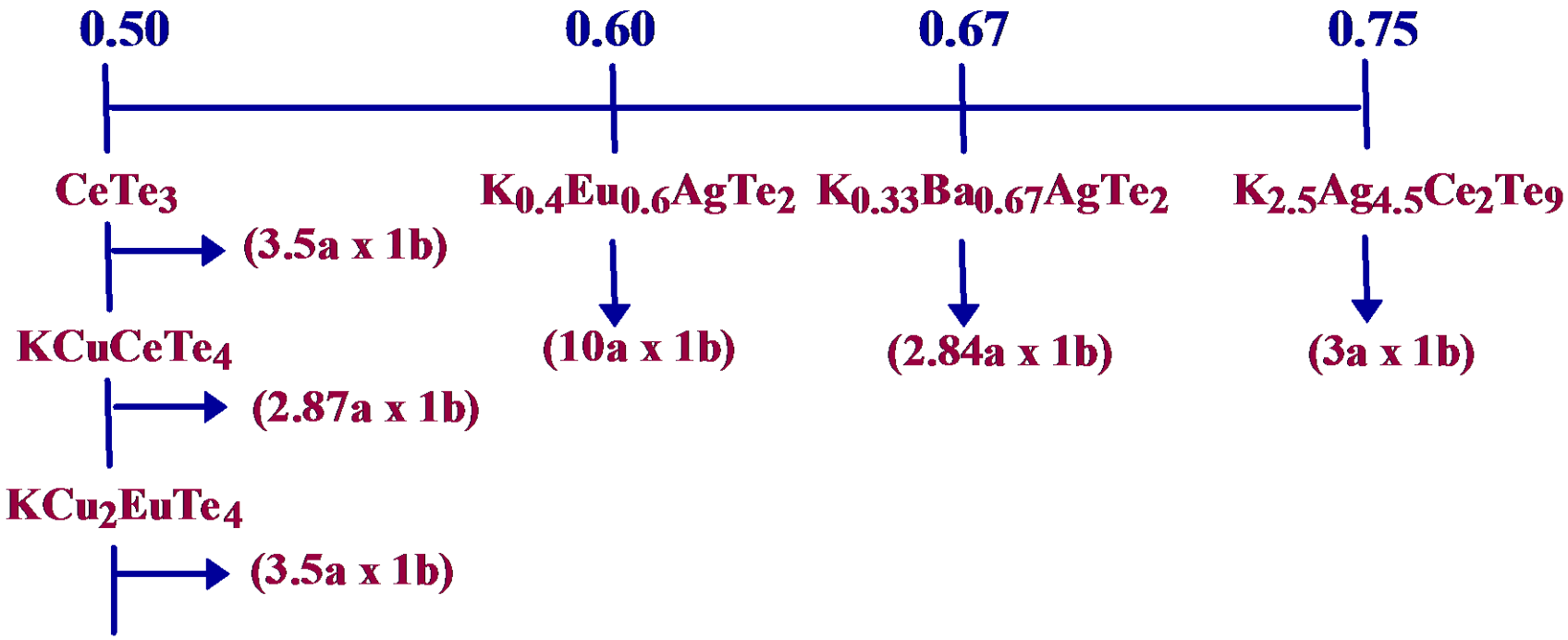
Radial distance r(Å)

Local structure: PDF versus Crystallography



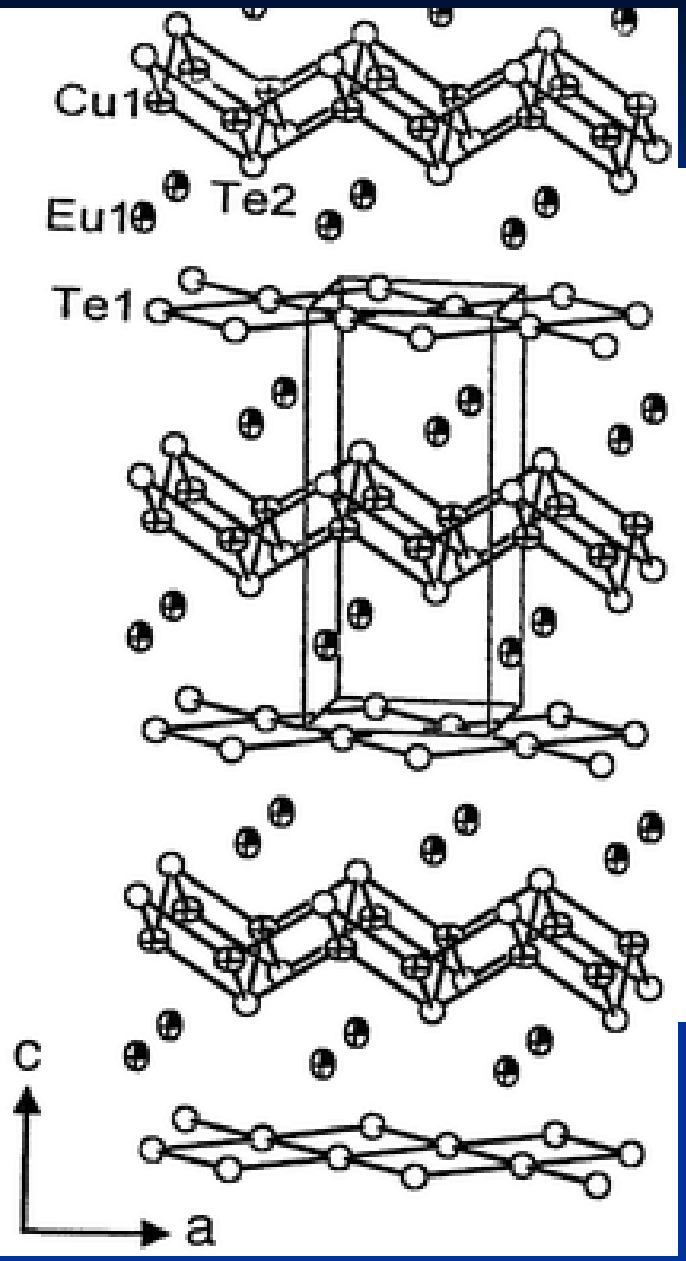


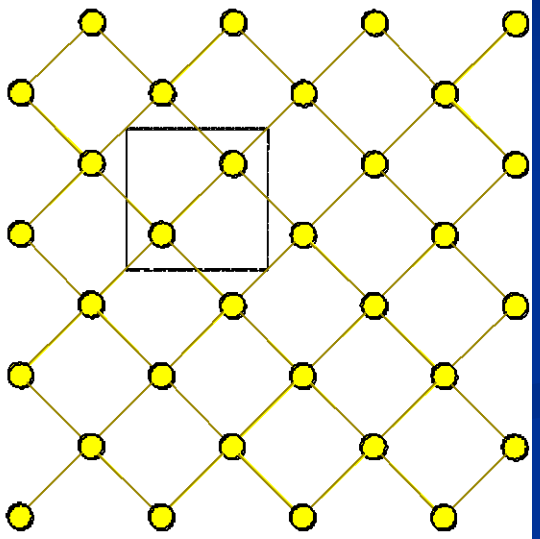
Correlation between charge and superlattice?



More square nets…

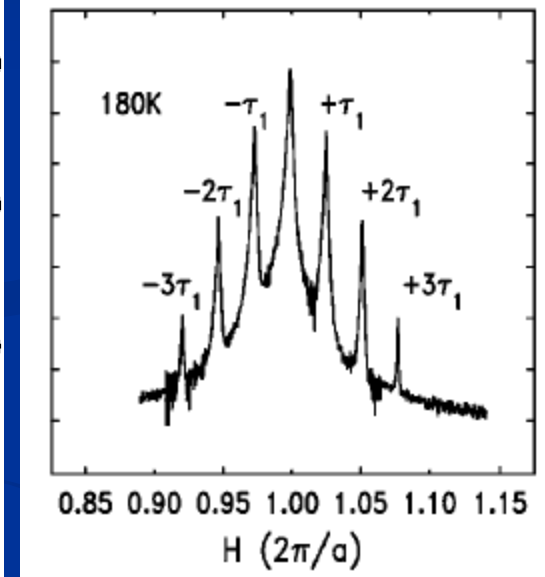
$LaAgSb_2$, $Cu_{0.66}EuTe_2$





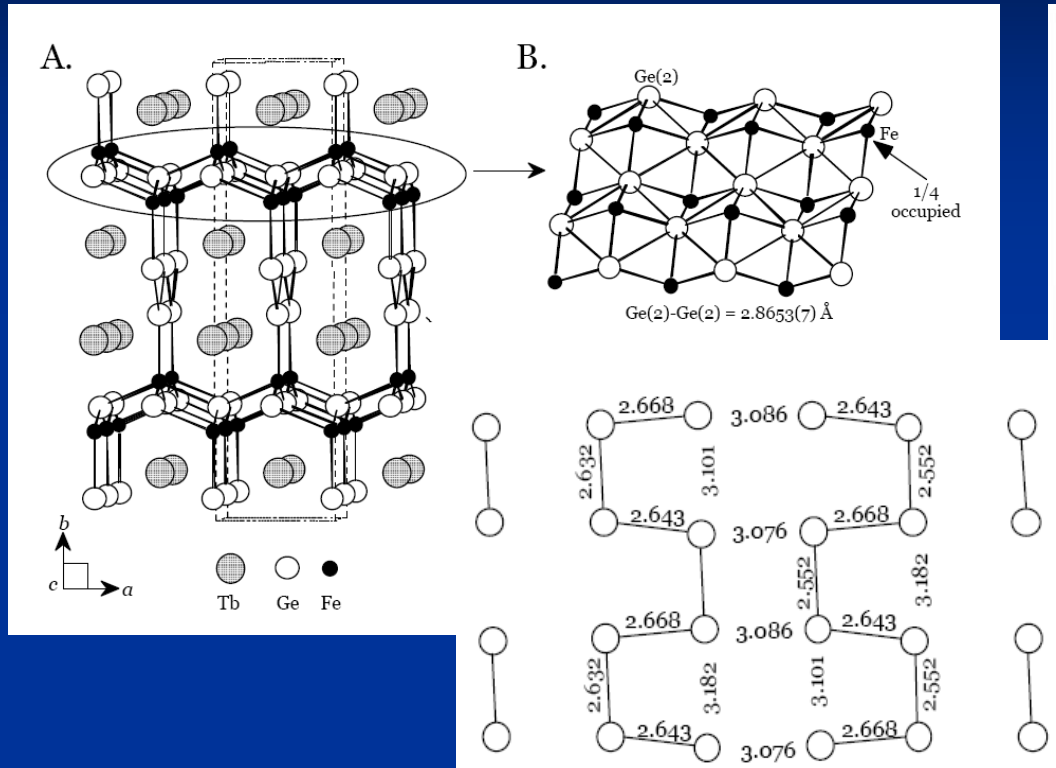
Sb square net
Sb^{2-} → Sb_2^{4-}

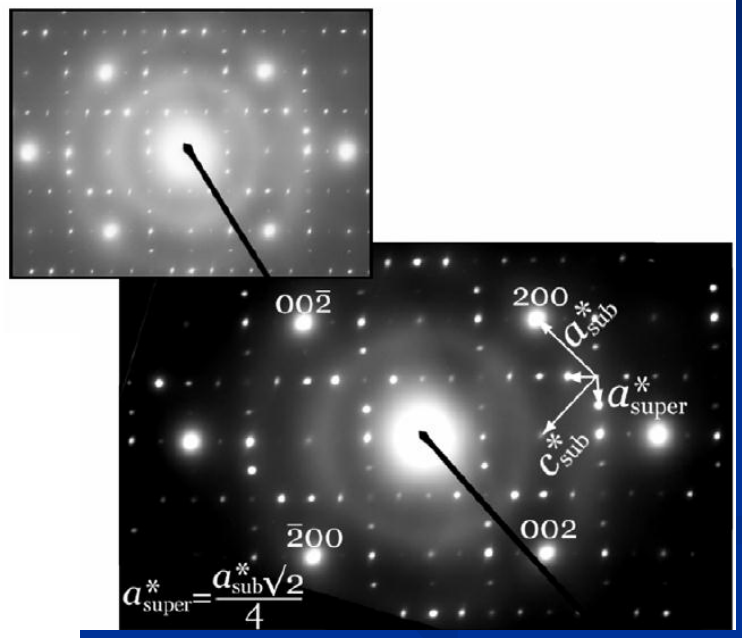
Reciprocal lattice scans of $LaAgSb_2$ around (1 0 7)



C. Song, Jaehyun Park, Japil Koo, and K.-B. Lee, J. Y. Rhee, S. L. Bud'ko, P. C. Canfield, B. N. Harmon, and A. I. Goldman, PHYSICAL REVIEW B **68**, 035113 ~2003.

Tb_4FeGe_8 (Ge-net)





Crystal system	Orthorhombic	Monoclinic
Space group	*Cmcm* (#63)	$P2_1/n$ (#14)
Unit cell dimensions (Å)	a = 4.1118(14)	a = 5.7315(11)
	b = 15.844(5)	b = 15.842(3); β = 91.724(4)°
	c = 3.9885(13)	c = 11.438(2) Å
Volume (Å^3)	259.84(15)	1038.1(4)

Conclusions

- Square nets inherently unstable
- Square nets of Te obey the octet rule.
- Permanent CDW materials a potential new source of narrow gap semiconductors
- New way to design extremely narrow gap materials
- Known modulated Te-net compounds need to be solved.
- Many “ideal” square net compounds need to be re-examined.