Superstructures in Polytelluride Compounds with Square Nets

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

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NSF
Peierls Distortion
one-dimensional system

Half-filled band unstable…
Opens energy gap

Roald Hoffmann
Peierls distortion

two-dimensional system

Examples:
Many tellurides, antimonides
Silicides etc  $\text{K}_{0.33}\text{Ba}_{0.66}\text{AgTe}_2$
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-poorman metal transition**

$\text{Te}^0$

Charge/Te atom: -2, -1, $-\frac{1}{2}$, $-\frac{1}{3}$, etc

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 superconductivity 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$_2$Te$_3$ 0.14 eV, CsBi$_4$Te$_6$ 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.
\[ \text{K}_{0.33}\text{Ba}_{0.66}\text{AgTe}_2 \]

Metallic!

Electrical properties and superstructure

\[ [K_{0.33}Ba_{0.66}]^{1.66^+} (AgTe)^{+}Te^{-0.66} \]

Predicts \( Te_3^{2-} \)

Semiconductor...
Trimers $(\text{Te}_3)^{2-}$, 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$_2^{2-}$

Distorted Net: band gap
KCuCeTe$_4$  

$\text{KCuTe(CeTe}_3\text{)}$

Bandgap = 0.32eV

$\alpha/S$ (arbitrary units)

Thermodynamic Sinks

\[ A_2\text{Te} + M_c + \text{Ln} + \text{Te} \xrightarrow{\text{phase separation}} \text{LnTe}_3 + M_c\text{Te} \]

NdTe$_3$

CuTe

NaCuTe
Electron Diffraction of KCuCeTe₄

KCuTe(CeTe₃)

(CeTe₃) = (CeTe)⁺(Te₂)⁻

(Te₂)⁻ = tetramers Te₄²⁻ (or Te₂²⁻/Te₆²⁻)

Electrical Conductivity

σ (S/cm)

Temperature (K)

Reciprocal Angstroms

Intensity/Arbitrary Units

(110)

0.348a⁺

(100)

0.348a⁺

(110)
“1a x 2.87b”  +  “1a x 2.87b”  rotated 90 deg  →  “2.87a x 2.87b”
KCu$_2$EuTe$_4$

\[ K^+, 2\text{Cu}^{1+}, \text{Eu}^{2+}, 2\text{Te}^{2-}, 2\text{Te}^{-0.5} \]

**Bandgap of Na$_{0.2}$Ag$_{2.8}$EuTe$_4**

Bandgap = 0.24 eV

**Electrical Conductivity**

\[ \sigma (\text{S/cm}) \]

\[ 0.10 \text{ to } 100.00 \]

Time (K)

\[ 0 \text{ to } 300 \]
[AMEuTe] □ divalent □ rare-earth meta

\[
\begin{align*}
2K_2Te + 1Cu + 1Eu + 7Te & \xrightarrow{850C/6d} KCu_2EuTe_4  \\
4Na_2Te + 3Ag + 1Eu + 16Te & \xrightarrow{850C/6d} Na_{0.2}Ag_{2.8}EuTe_4
\end{align*}
\]

<table>
<thead>
<tr>
<th>Formula</th>
<th>KCu\textsubscript{2}EuTe\textsubscript{4}</th>
<th>Na\textsubscript{0.2}Ag\textsubscript{2.8}EuTe\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>(P\ 4mm)</td>
<td>(P4mm)</td>
</tr>
<tr>
<td>a, □</td>
<td>4.4365(6)</td>
<td>4.4573(6)</td>
</tr>
<tr>
<td>c, □</td>
<td>11.365(2)</td>
<td>11.112(2)</td>
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<tr>
<td>V, □\textsuperscript{3}</td>
<td>223.69(6)</td>
<td>220.78(6)</td>
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<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>R/wR2</td>
<td>7.3/17.8</td>
<td>6.8/18.8</td>
</tr>
<tr>
<td>Goof</td>
<td>1.198</td>
<td>1.077</td>
</tr>
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</table>
KCu$_2$EuTe$_4$ $^{2/7}a$- supercell
**KCu₂EuTe₄**: Elemental Substitution of □Cu□ with □Ag

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

\[
\text{KCu}_2\text{EuTe}_4 \xrightarrow{-35\% \text{ K and } +35\% \text{ Eu}} K_{0.65}Ag_2Eu_{1.35}Te_4
\]

<table>
<thead>
<tr>
<th>crystal data</th>
<th>KCu₂EuTe₄</th>
<th>K₀.₆₅Ag₂Eu₁.₃₅Te₄</th>
</tr>
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<tbody>
<tr>
<td>Space group</td>
<td>P4mm</td>
<td>Abm2</td>
</tr>
<tr>
<td>a, Å</td>
<td>4.4365(6)</td>
<td>4.4989(9)</td>
</tr>
<tr>
<td>b, Å</td>
<td>4.4365(6)</td>
<td>45.279(9)</td>
</tr>
<tr>
<td>c, Å</td>
<td>11.365(2)</td>
<td>22.799(5)</td>
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<tr>
<td>V, Å³</td>
<td>223.69(6)</td>
<td>4644(1)</td>
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<tr>
<td>Z</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>R1/wR2</td>
<td>7.3/17.8</td>
<td>6.46/27.80</td>
</tr>
<tr>
<td></td>
<td>1a x 7b supercell</td>
<td>1a x 10b x 2c supercell</td>
</tr>
</tbody>
</table>
$K_{0.65}Ag_2Eu_{1.35}Te_4$, $1a \times 10b \times 2c$ supercell, $A\text{ bm}2$
Distorted net in $K_{0.65}Ag_2Eu_{1.35}Te_4$

$Te^{2-}_3$ trimers

$Te^{-0.67}$ vs $Te^{-0.60}$
$K_{2.5}Ag_{4.5}Te_3(CeTe_3)_2$
**K_{2.5}Ag_{4.5}La_2Te_9** and **K_{2.5}Ag_{4.5}Ce_2Te_9**

<table>
<thead>
<tr>
<th>Subcell</th>
<th>Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = 4.4844(9) Å</td>
<td>a' = 14.130(3) Å</td>
</tr>
<tr>
<td>b = 4.5116(9) Å</td>
<td>b' = 50.441(10) Å</td>
</tr>
<tr>
<td>c = 50.859(10) Å</td>
<td>c' = 4.4492(9) Å</td>
</tr>
<tr>
<td>α = 90°</td>
<td>α = 90°</td>
</tr>
<tr>
<td>β = 90°</td>
<td>β = 108.37(3)°</td>
</tr>
<tr>
<td>γ = 90°</td>
<td>γ = 90°</td>
</tr>
<tr>
<td>I mm m</td>
<td>C 2/m</td>
</tr>
</tbody>
</table>

(A) [Image of crystal structure]

(B) [Image of crystal structure]

Graph:

\[ y = 93.2 \cdot e^{-335x}, \quad R = 0.99845 \]

Bandgap \( E_g = 0.0577 \text{ eV} \)
What about RETe$_3$?

- RETe$_3$ adopt the NdTe$_3$ structure type ($C mcm$)
  - $(\text{NdTe})^+(\text{Te}^{-0.5})_2$
- Square Te nets
- TEM studies on SmTe$_3$ showed 3.5-fold superstructures: proposed trimers Te$_3^{2-}$
- LaTe$_2$
  - $(\text{LaTe})^+(\text{Te}^{-1})$ (superstructure has Te$_2^{2-}$ dimers)
- DySe$_{1.84}$ was shown to posses a 66-fold superstructure (Lee et al)
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.

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.

**Crystal Data**
- Orthorhombic Cmcm (#63)
- $a = 4.3800(12)$ Å
- $b = 26.056(7)$ Å
- $c = 4.3976(12)$ Å
- $R_f/wR_f [I-2\sigma(I)] = 1.64/4.22$
Transmission Electron Microscopy (TEM) study

Selected area electron diffraction pattern of CeTe$_3$ at the [010], orientation showing the $7c_{\text{sub}}$ superlattice.

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

Selected area electron diffraction pattern of CeTe$_3$ at the [100], orientation (cross section). There is no modulation along the b$^*$ direction since there are no supplementary supercell spots.

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

Crystal Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$R_1/wR_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeTe$_3$</td>
<td>RETe$_3$</td>
<td>30.800(8)</td>
<td>26.055(7)</td>
<td>4.3810(12)</td>
<td>3.82/8.83</td>
</tr>
<tr>
<td>PrTe$_3$</td>
<td>RETe$_3$</td>
<td>30.640(8)</td>
<td>25.915(7)</td>
<td>4.3598(11)</td>
<td>4.98/14.69</td>
</tr>
<tr>
<td>NdTe$_3$</td>
<td>RETe$_3$</td>
<td>30.561(6)</td>
<td>25.859(5)</td>
<td>4.3563(9)</td>
<td>4.81/12.43</td>
</tr>
<tr>
<td>SmTe$_3$</td>
<td>RETe$_3$</td>
<td>30.383(8)</td>
<td>25.676(6)</td>
<td>4.3341(11)</td>
<td>5.30/20.28</td>
</tr>
<tr>
<td>GdTe$_3$</td>
<td>RETe$_3$</td>
<td>30.307(7)</td>
<td>25.573(6)</td>
<td>4.3162(9)</td>
<td>5.44/10.54</td>
</tr>
</tbody>
</table>
Resolving the Distortion in RETe$_3$

The supercell has a c=7c$_{sub}$ axis. The modulation is mostly located in the Te net which results in 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.

**Crystal Data**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ama2 (#40)</th>
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<td>25.573(6) Å</td>
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<tr>
<td>c</td>
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<td>4.3598(11) Å</td>
<td>4.3563(9) Å</td>
<td>4.3341(11) Å</td>
<td>4.3162(9) Å</td>
</tr>
<tr>
<td>R$_1$/wR$_2$</td>
<td>3.82/8.83</td>
<td>4.98/14.69</td>
<td>4.81/12.43</td>
<td>5.30/20.28</td>
<td>5.44/10.54</td>
</tr>
</tbody>
</table>

- CeTe$_3$
- PrTe$_3$
- NdTe$_3$
- SmTe$_3$
- GdTe$_3$
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

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
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 $\rightarrow$ (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 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

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

\[ \pi \sin(\theta) / \lambda = 1.0135 \sin(\theta) \]

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

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

\[ G(r) \sim 1D \text{ Patterson function} \]

\[ G(r) = 4\pi r [\rho(r) - \rho_o] \]

\( \rho(r) \) is the local and \( \rho_o \) the average atomic density

Billinge, Egami
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.
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.
Local structure: PDF versus Crystallography
Correlation between charge and superlattice?

0.50
CeTe₃
KCuCeTe₄
KₐCe₂Te₄

0.60
K₀.₄Eu₀.₆AgTe₂
(10a x 1b)

0.67
K₀.₃₃Ba₀.₆₇AgTe₂
(2.8₄a x 1b)

0.75
K₂.₅Ag₄.₅Ce₂Te₉
(3a x 1b)
More square nets...

LaAgSb$_2$, Cu$_{0.66}$EuTe$_2$

Reciprocal lattice scans of LaAgSb$_2$ around (1 0 7)

Sb square net

Sb$^{2-}$ $\rightarrow$ Sb$_2^{4-}$

**Tb$_4$FeGe$_8$ (Ge-net)**

**Crystal system**: Orthorhombic

**Space group**: $C_{mcm}$ (#63)

**Unit cell dimensions (Å)**

- $a = 4.1118(14)$
- $b = 15.844(5)$
- $c = 3.9885(13)$

**Volume (Å$^3$)**

- $259.84(15)$

**Monoclinic**

- $P_{21}/n$ (#14)

- $a = 5.7315(11)$
- $b = 15.842(3)$; $\beta = 91.724(4)^\circ$
- $c = 11.438(2)$ Å

- $1038.1(4)$
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.