# Transport Coefficients with WIEN2k

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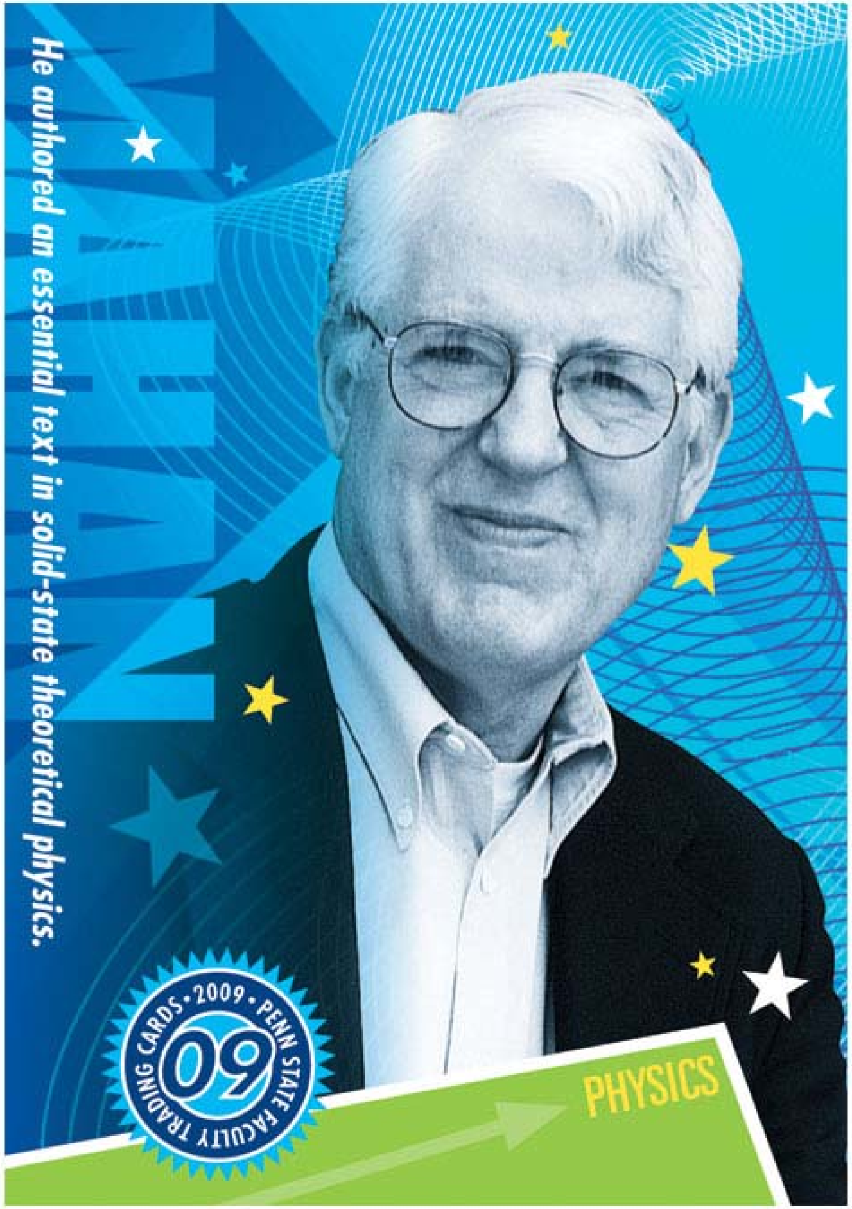
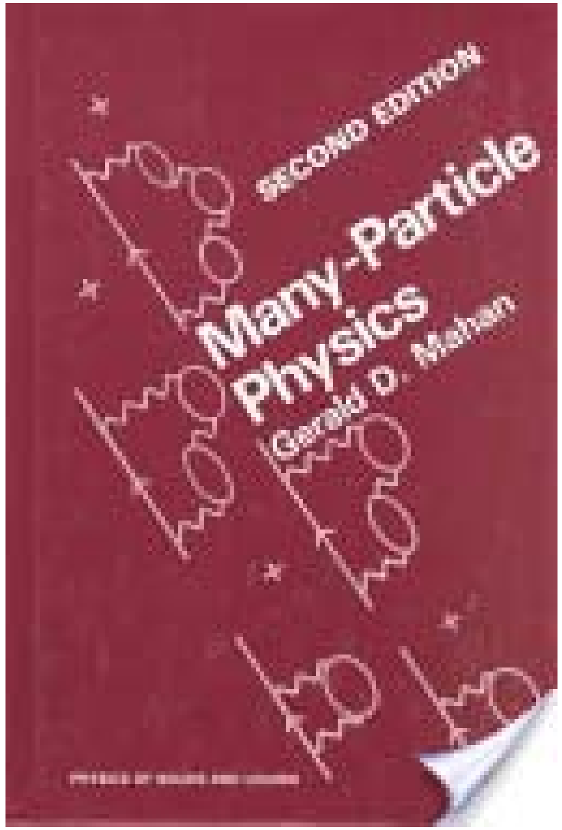
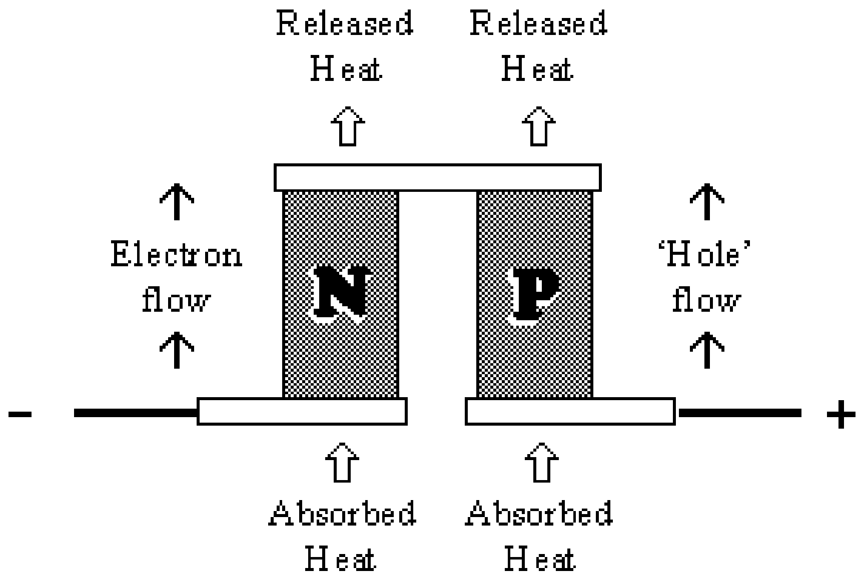


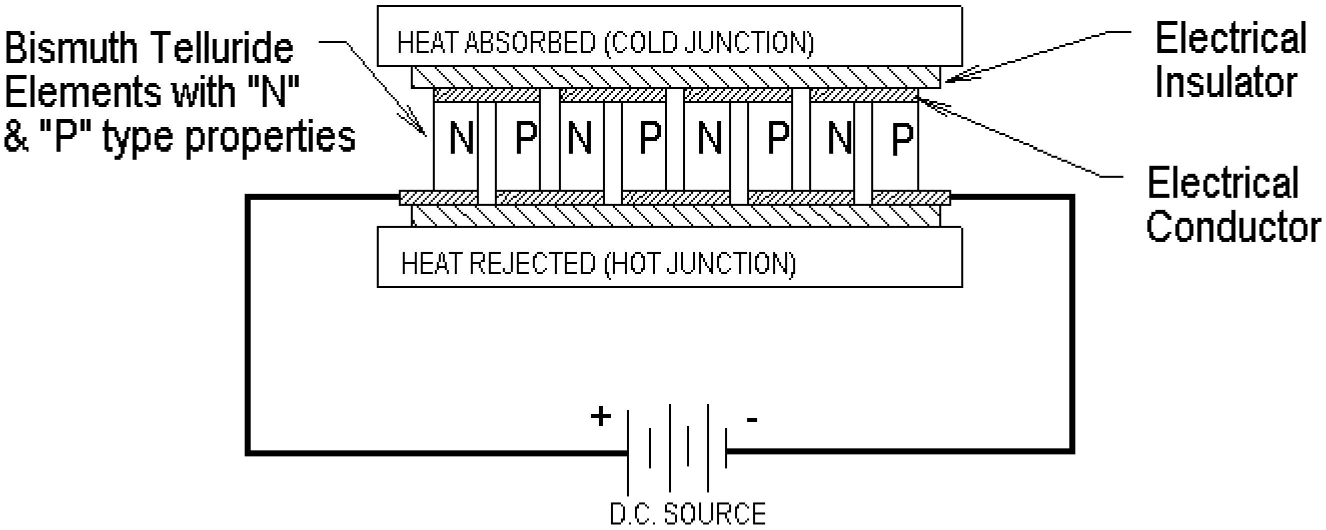

marlow
industries, inc.

MRI

# Thermoelectrics



# Thermoelectrics



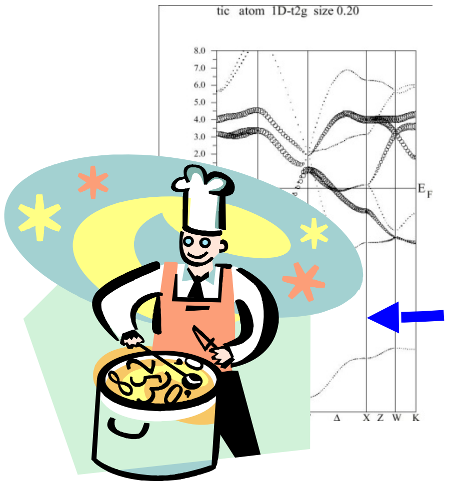

Elements Electrically in series & thermally in parallel

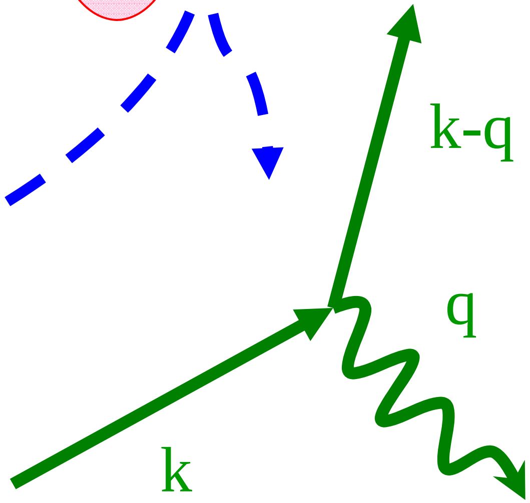
$$Z = \frac{\sigma S^2}{\kappa}$$

# Conductivity 101

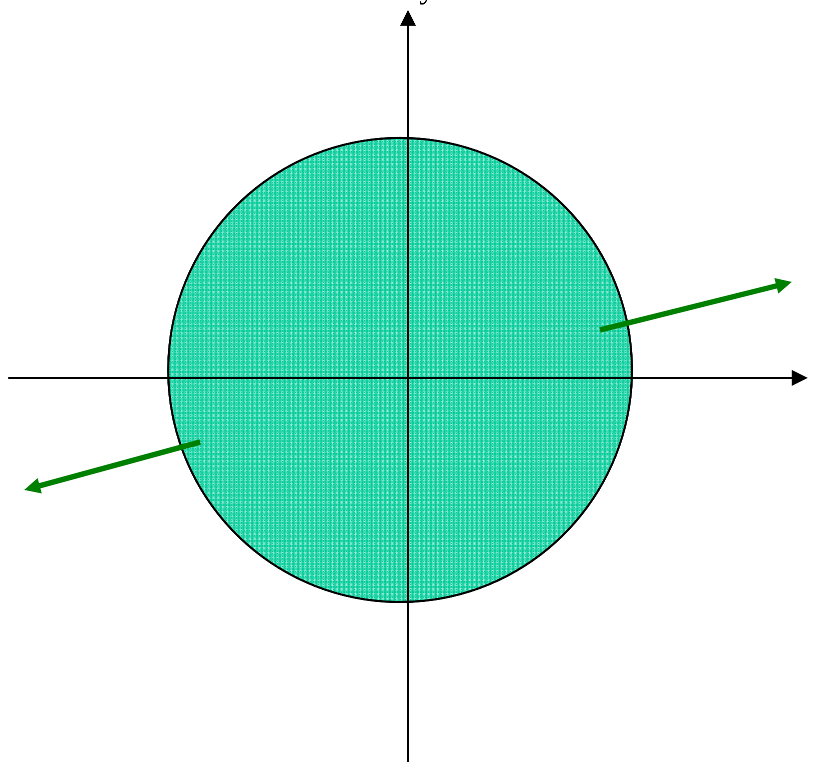
*Drude et al.*

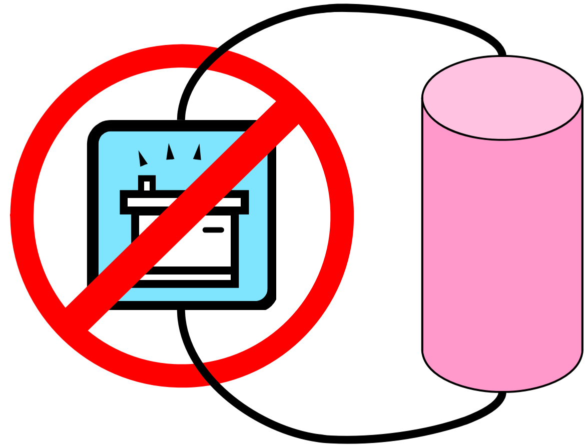
$$\sigma = e^2 \frac{n}{m} \tau$$



# Conductivity 101



$$J = e\sum_k f_0(\varepsilon_k)\, v_k = 0$$

$$J = e\sum_k f_k\, v_k \neq 0$$

# Conductivity 101

$$\vec{J} = e\sum_k f_k \vec{v}_k$$

$$\vec{J} = \overleftrightarrow{\sigma} \cdot \vec{E}$$

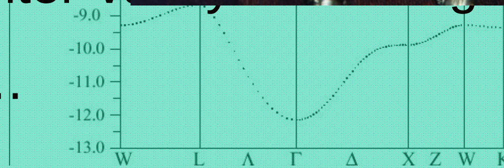
$$f_k = f^0(\varepsilon_k) + e\left(-\frac{\partial f^0}{\partial \varepsilon}\right)\tau_k \, \vec{v}_k \cdot \vec{E}$$

$$\vec{J} = \left[ e^2 \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \tau_k \, \vec{v}_k \vec{v}_k \right] \cdot \vec{E}$$

# Conductivity 2k

$$\overleftrightarrow{\sigma} = e^2 \sum_k \left(-\frac{\partial f^0}{\partial \varepsilon}\right)\tau_k \vec{v}_k \vec{v}_k$$

$$\vec{v}_k = \frac{1}{\hbar}\frac{\partial \varepsilon_k}{\partial \vec{k}} \qquad \frac{1}{m}\vec{p}_k = \frac{1}{m}\left\langle k\right|\hat{\vec{p}}\left|\right.$$




First Bo

- Acoust
- Optical non-pol
- Ionized
- Inter-va
- …

# Careful…

- Doping: rigid band
- Gap problem
- Temperature dependence of the electronic structure.
- Alloys. Single site approximations do not work.
- Many k-points

# For free…

$$J = \sigma E - \sigma S \nabla T$$

$$J_Q = \sigma S T E - \kappa \nabla T$$

$$\overleftrightarrow{\sigma} = e^2 \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k$$

$$S = \frac{e k_B}{\sigma} \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k \ \frac{(\varepsilon_k - \mu)}{k_B T}$$

$$\kappa_{el} = k_B^2 \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k \left[ \frac{(\varepsilon_k - \mu)}{k_B T} \right]^2$$

# Application to Thermoelectrics

$$Z = \frac{\sigma S^2}{\kappa_{el} + \kappa_{ph}}$$

# Transport Distribution

$$\vec{\vec{\sigma}} = e^2 \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k = e^2 \int d\varepsilon \ \Sigma(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right)$$

$$S = \frac{ek_B}{\sigma} \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k \ \frac{(\varepsilon_k - \mu)}{k_B T} = \frac{ek_B}{\sigma} \int d\varepsilon \ \Sigma(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \frac{(\varepsilon - \mu)}{k_B T}$$

$$\kappa_{el} = k_B^2 \sum_k \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \tau_k \ \vec{v}_k \vec{v}_k \left[ \frac{(\varepsilon_k - \mu)}{k_B T} \right]^2 = k_B^2 \int d\varepsilon \ \Sigma(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \left[ \frac{(\varepsilon_k - \mu)}{k_B T} \right]^2$$

# Application to Thermoelectrics: The best thermoelectric

$$Z = \frac{\sigma S^2}{\kappa_{el} + \kappa_{ph}} = Z[\Sigma]$$

$$\Sigma_{best} \Big/ \max_{\Sigma} Z[\Sigma] = Z[\Sigma_{best}]$$

$$\Sigma_{best}(\varepsilon) = C\delta(\varepsilon - \varepsilon_0)$$

$$\varepsilon_0 \approx 2.4 k_B T$$

# Transport Distribution

$$\Sigma(\varepsilon) = \sum_k \tau_k \vec{v}_k \vec{v}_k \delta(\varepsilon_k - \varepsilon)$$

$$N(\varepsilon) = \int dS \frac{1}{|\nabla \varepsilon_k|}$$

$$= N(\varepsilon) v^2(\varepsilon) \tau(\varepsilon)$$

$$v(\varepsilon) = \nabla \varepsilon_k$$

$$\Sigma_{best}(\varepsilon) = C\delta(\varepsilon - \varepsilon_0)$$

$$\varepsilon_0 \approx 2.4 k_B T$$

# Band transport

Georg Madsen

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University of Aarhus

iNANO

MRI

# Program: BoltzTraP

Smoothed Fourier expansion of band energies

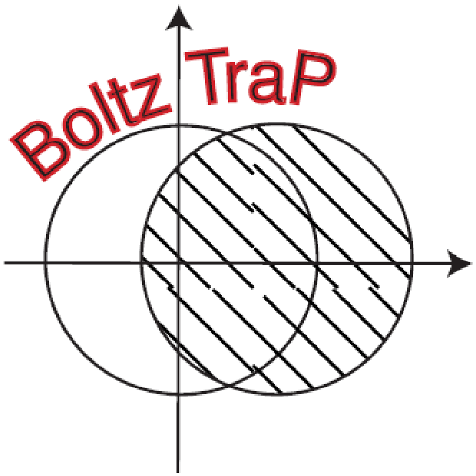
$$\varepsilon_i(\mathbf{k}) = \sum_{\mathbf{R}} \frac{1}{n_{\mathbf{R}}} c_{\mathbf{R},i} e^{i\mathbf{k}\cdot\mathbf{R}}$$

Pickett, Krakauer, Allen, PRB **38**, 2721

$$\frac{\partial \varepsilon_{i,\mathbf{k}}}{\partial k_\alpha} = \sum_{\mathbf{R}} \frac{i\mathbf{R}_\alpha}{n_{\mathbf{R}}} c_{\mathbf{R},i} e^{i\mathbf{k}\cdot\mathbf{R}}$$

Transport distribution

$$\sigma(\varepsilon) = \frac{1}{N} \sum \sigma_{i,\mathbf{k}} \frac{\delta(\varepsilon - \varepsilon_{i,\mathbf{k}})}{d\varepsilon}$$

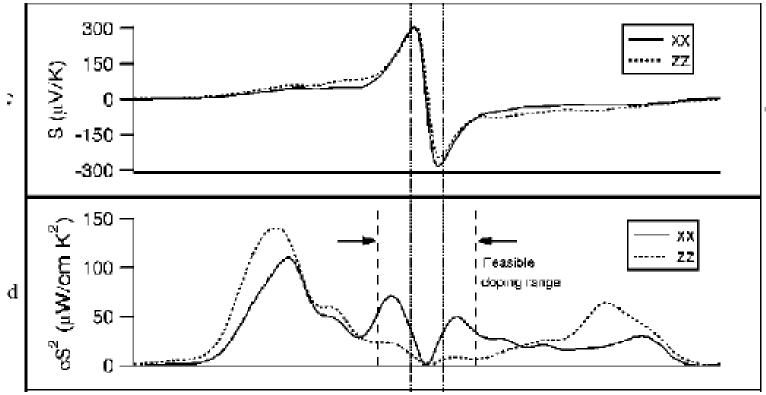



Rigid band approach

$$\sigma(\mu, T) = \int \sigma(\varepsilon) \left[ -\frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon} \right] \mathrm{d}\varepsilon$$

http://www.chem.au.dk/~webuorg/new/groups/gm/BoltzTrap/BoltzTrap.html

# Testing BoltzTraP. $Bi_2Te_3$

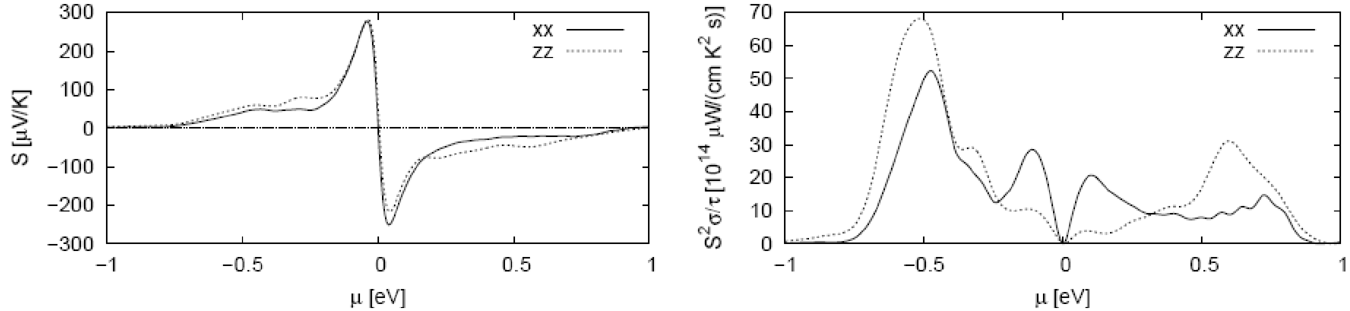



Calculate group velocities from momentum matrix elements.

$$v_\alpha(i,\mathbf{k}) = \frac{1}{m_e}\langle\psi(i,\mathbf{k})|\hat{p}_\alpha|\psi(i,\mathbf{k})\rangle$$

Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, Sofo *Phys. Rev. B* **68**, p125210

BoltzTraP:




Madsen, Singh, Comp. Phys. Commun. **175**, p67

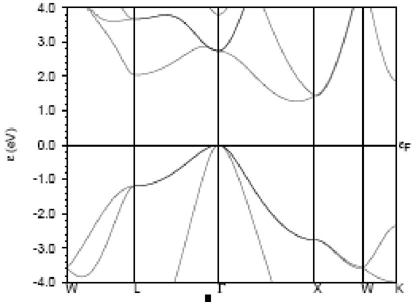
# The Grand Search

L/APW+lo, DFT

Spin orbit coupling (incl. $p_{1/2}$)

Efficient

All space groups



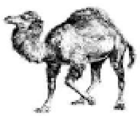

DCSC, SDU Odense

960 node PIV cluster

Semiclassic equations

Efficient: FFT, blas

Full conductivity tensors



Inorganic Crystal Structure Database

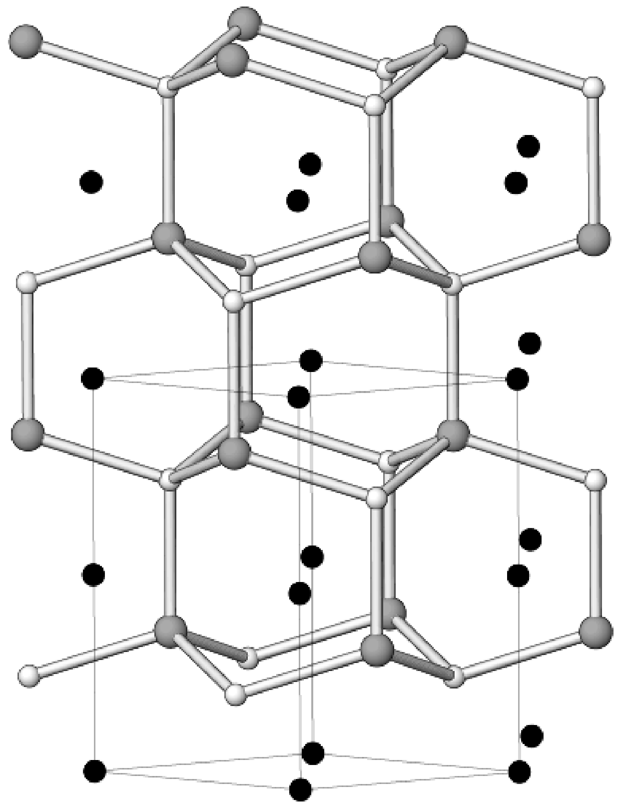
All known inorganic crystal structures

# TGS + BoltzTrap

| Formula | $E_g$ [eV] | $T$ [K] | $n$ [e/u.c.] | $zT$ |
|---|---|---|---|---|
| LiZnSb | 0.13 (PBE) | 150 | -0.03/ -0.02 | 0.14/ 0.25 |
| 44903 | 0.62 (EV) | 300 | -0.02/ -0.01 | 0.58/ 0.89 |
| 42064 | | 600 | -0.01/ -0.01 | 1.84/ 2.36 |
| ZnSb | 0.13 (PBE) | 150 | -0.00/ -0.01 | 0.07/ 0.06 |
| 76937 | 0.45 (EV) | 300 | -0.01/ -0.02 | 0.30/ 0.30 |
| | | 600 | -0.02/ -0.01 | 0.85/ 1.12 |
| ZnSb | 0.05 (PBE) | 150 | -0.01/ -0.01 | 0.06/ 0.08 |
| 43653 | 0.43 (EV) | 300 | -0.01/ -0.01 | 0.26/ 0.35 |
| | | 600 | -0.03/ -0.02 | 0.68/ 1.14 |
| $TlZn_2Sb_2$ | 0.00 (PBE) | 150 | -1.55/ -1.71 | 0.01/ 0.01 |
| 76499 | 0.00 (EV) | 300 | -1.53/ -1.69 | 0.02/ 0.05 |
| | | 600 | -1.49/ -1.66 | 0.06/ 0.13 |

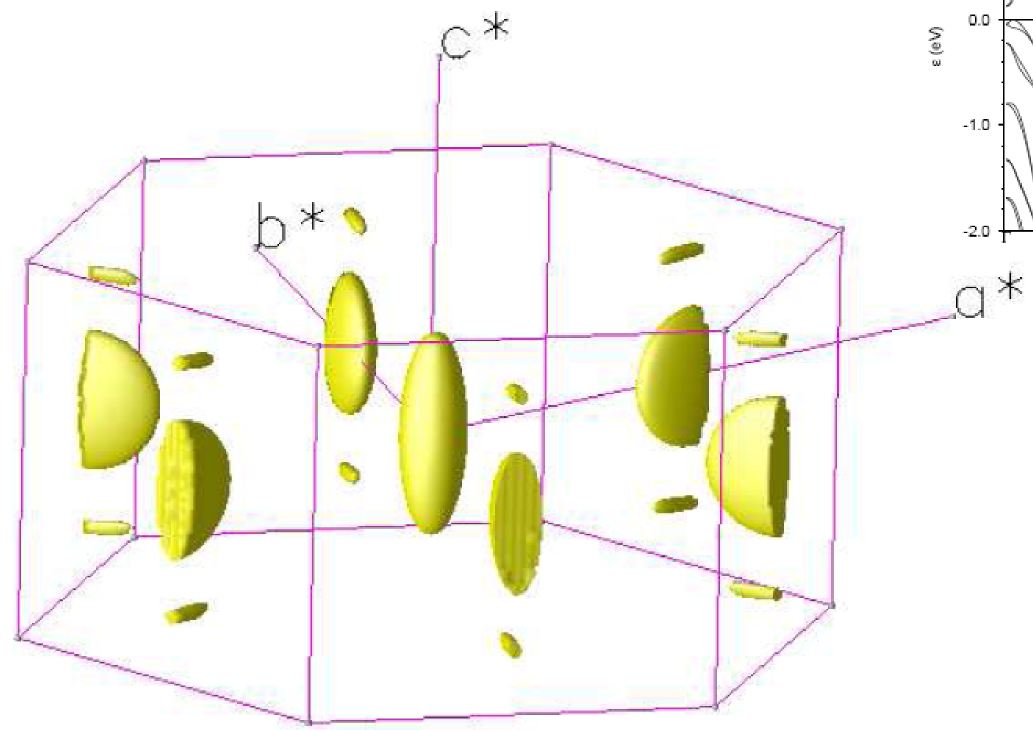
OBS $\kappa_l = 2$ W/mK, $\tau = 2 \times 10^{-14}$ s

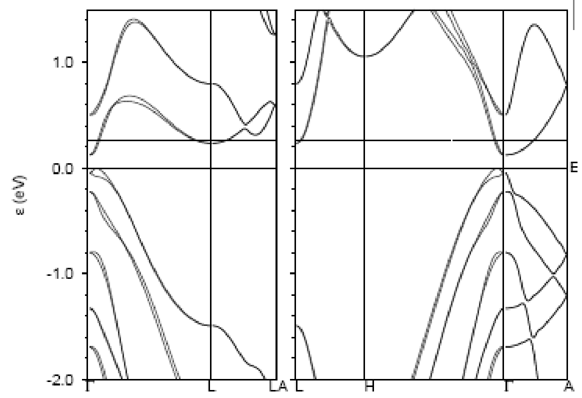
# LiZnSb structure



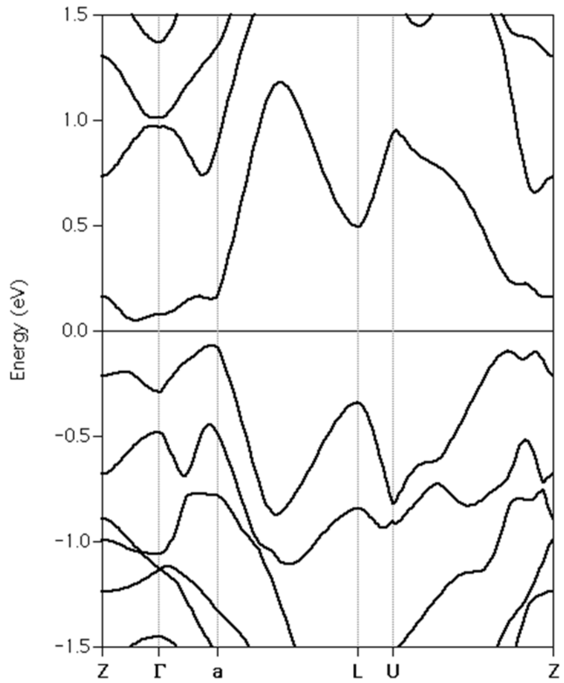
Li: Black spheres. Zn: White spheres. Sb: Grey spheres.

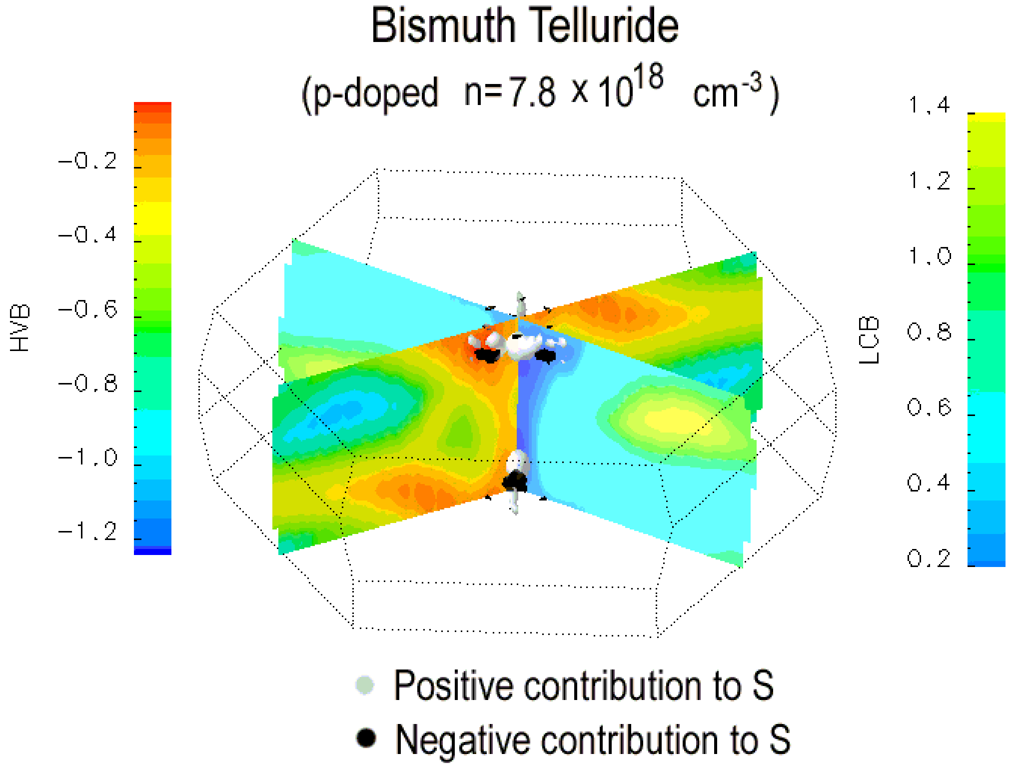
# LiZnSb Fermi-surface



# $Bi_2Te_3$

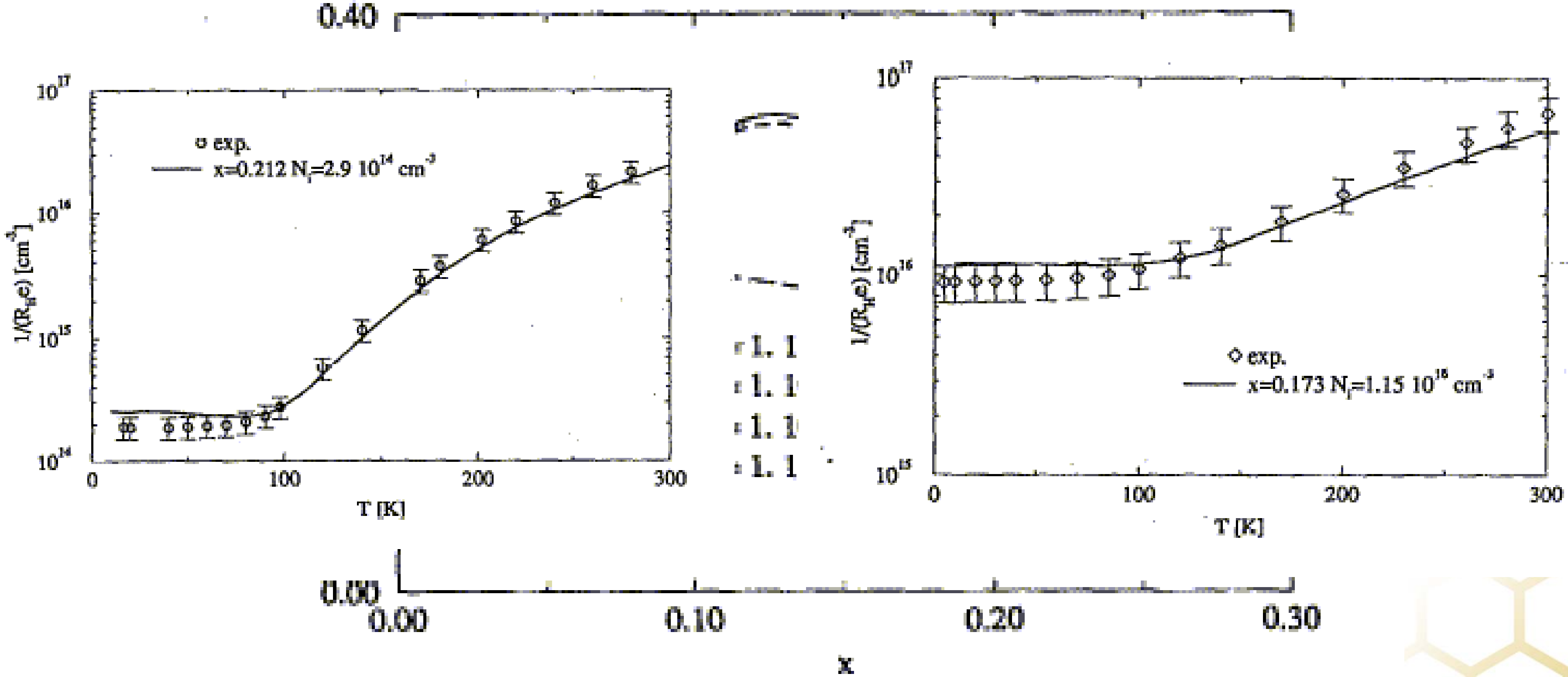

1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
Energy (eV)
Z
Γ
a
L
U
Z


Bismuth Telluride
(p-doped n=7.8 x 10^18 cm^-3)
HVB
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
LCB
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Positive contribution to S
Negative contribution to S

# Transport coefficients and thermoelectric figure of merit of $n$-$Hg_{1-x}Cd_xTe$

J. O. Sofo and G. D. Mahan
*Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6030, and Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200*

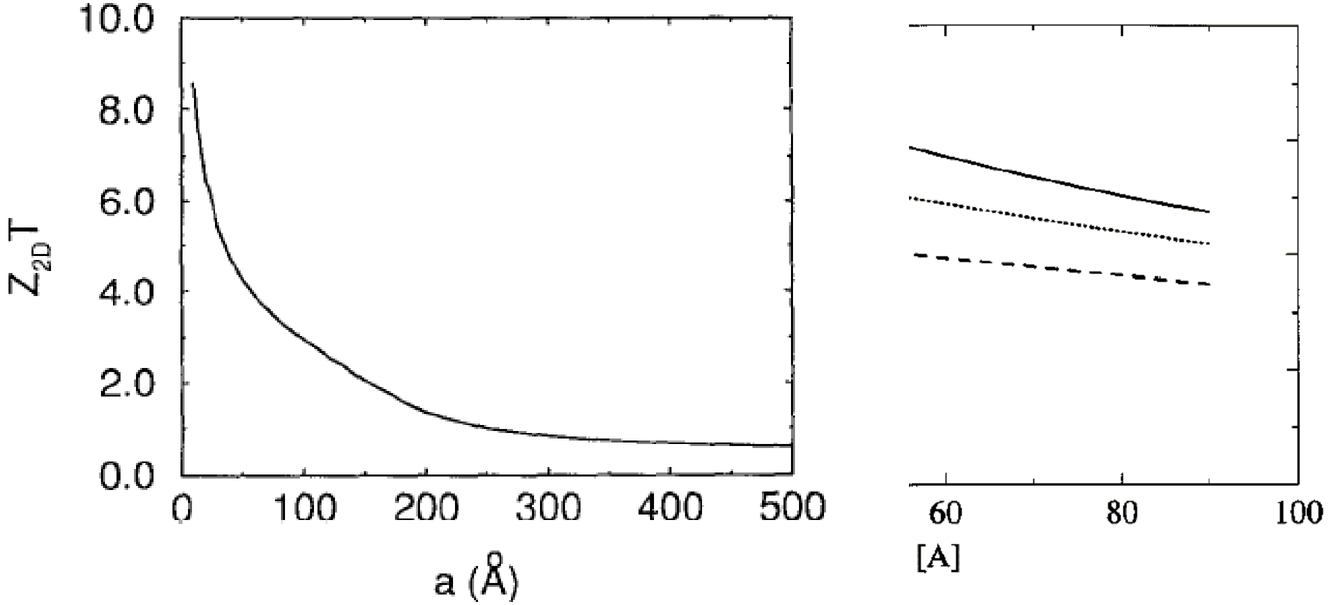
J. Baars
*Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, D-79108 Freiburg, Germany*



# Thermoelectric figure of merit of superlattices

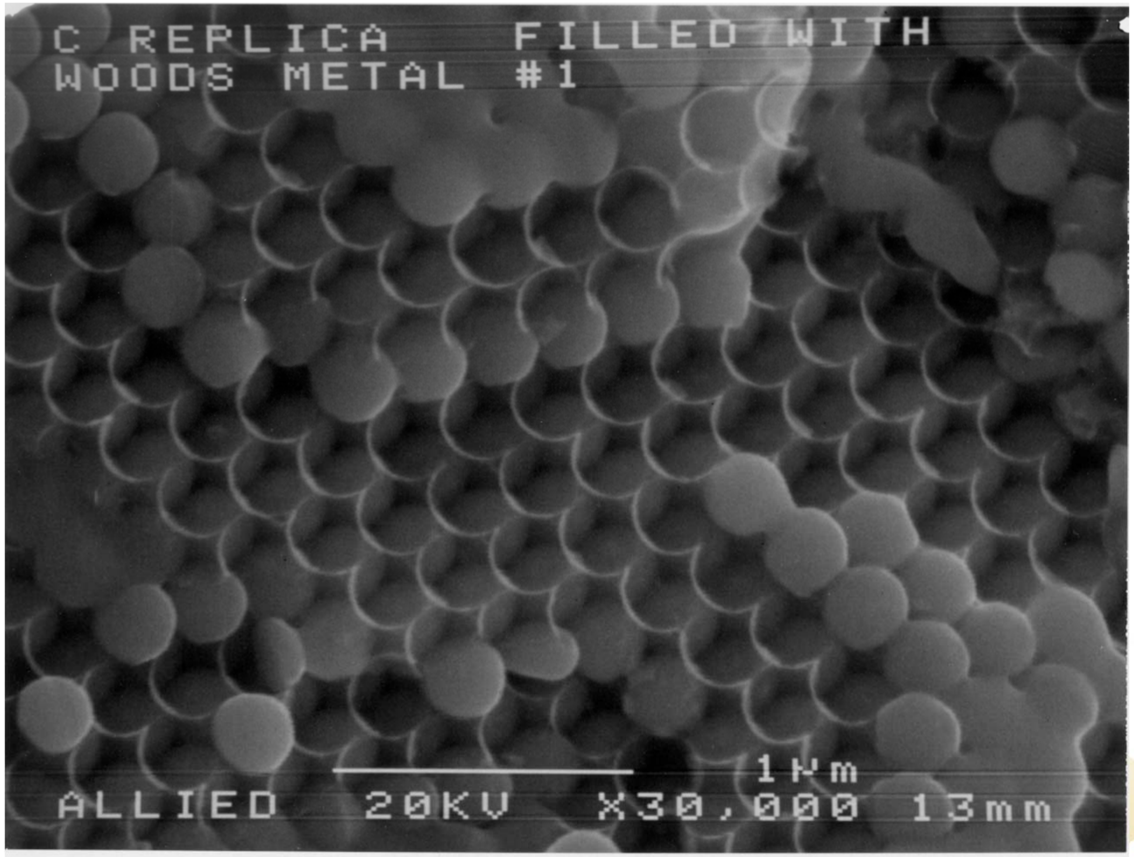
J. O. Sofo and G. D. Mahan
*Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6030, and Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200*

2690 Appl. Phys. Lett. 65 (21), 21 November 1994



# Opals

- Different scattering for phonons and electrons.
- Work done for Allied Signal Corp.
- Not an alternative…
- ☹



# Summary

- Tool to explore new compounds, pressure, “negative” pressure.
- Prediction of a new compound by G. Madsen.
- Easy to expand adding new Scattering Mechanisms
- Limited applications to “non-correlated” semiconductors.

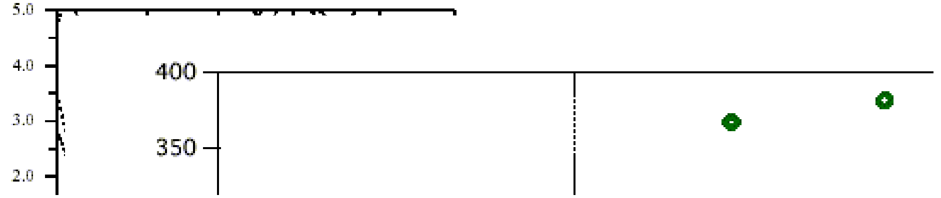
# Collaborators

- Claudia Ambrosch-Draxl (UNI-GRAZ)
- Georg Madsen
- John Badding (Penn State)
- Timo Thonhauser (Wake Forest)
- Tom Scheidemantel (Penn State)

With the always present coaching of Jerry Mahan.


DON'T
EVER
GIVE UP
joe-ks.com

# Bismuth

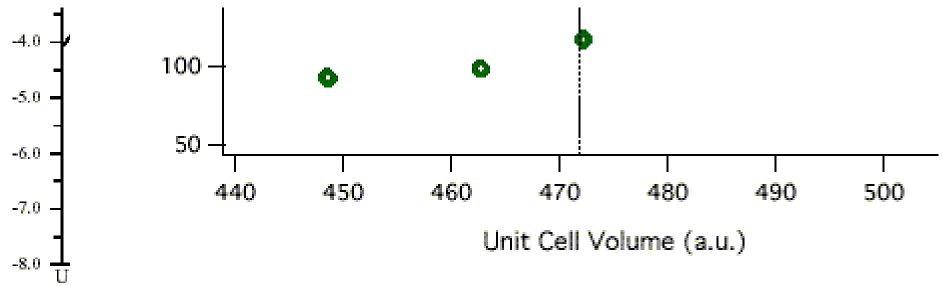



JOURNAL OF APPLIED PHYSICS VOLUME 34, NUMBER 1 JANUARY 1963

**Transport Properties of Bismuth Single Crystals**

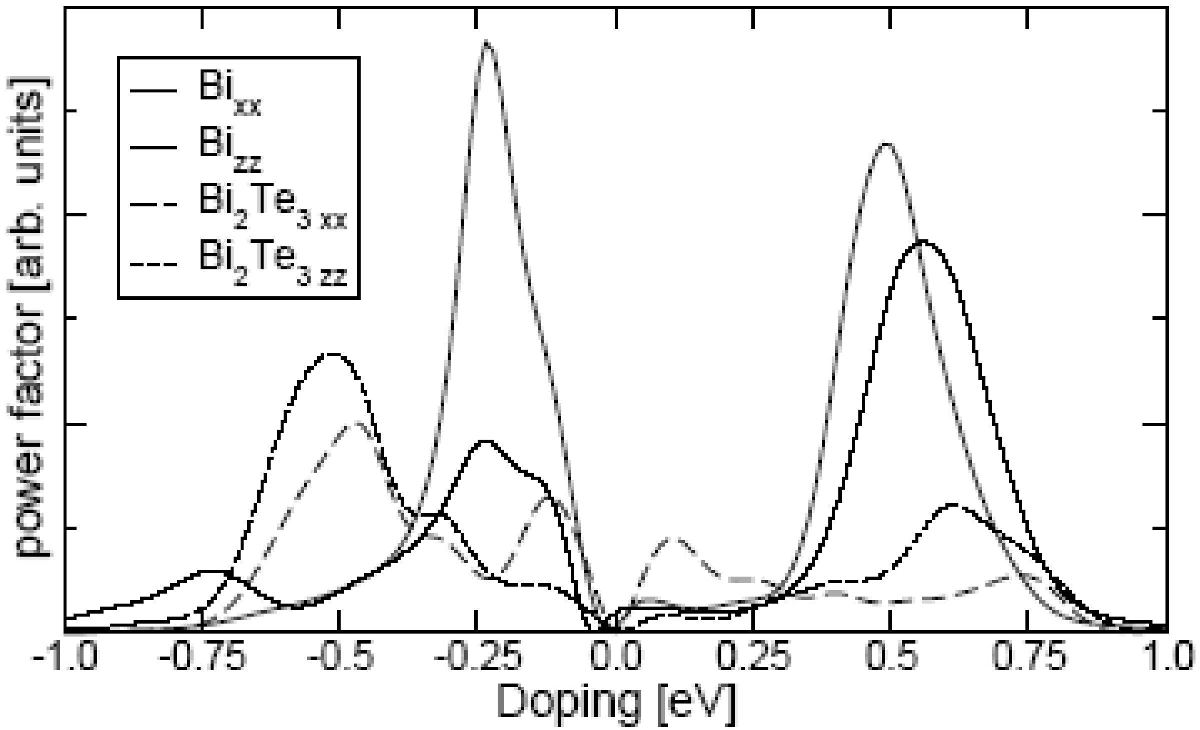
C. F. GALLO, B. S. CHANDRASEKHAR, AND P. H. SUTTER
*Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania*

(Received 11 June 1962)



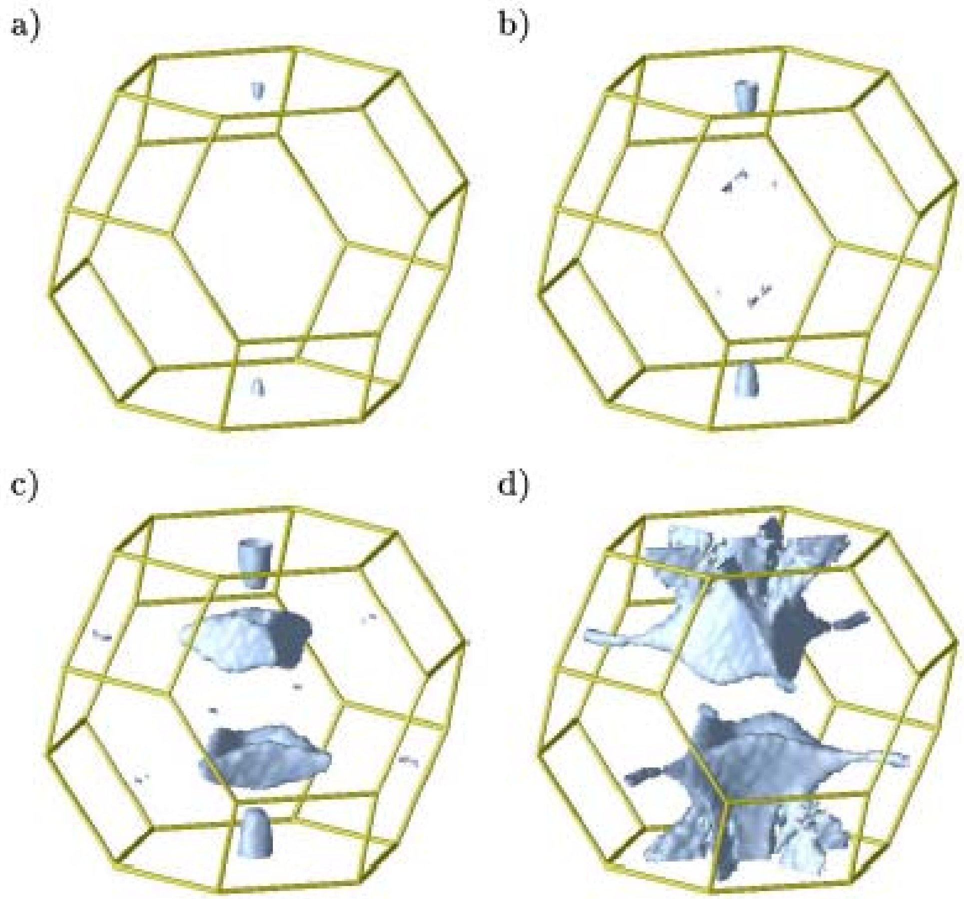

MRI

# Bi vs. $Bi_2Te_3$




Thonhauser, Scheidemantel, Sofo, Appl. Phys. Lett. 2004

# Why is Bi so good?



# Is there any hope?