Electrons and holes in bismuth
A list of answered and unanswered questions

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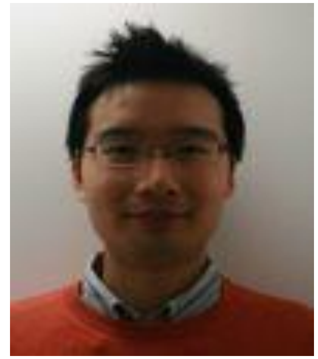

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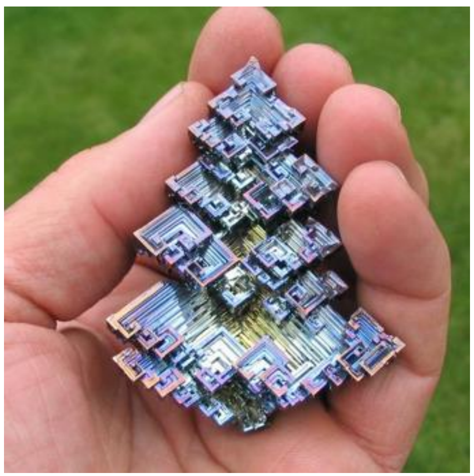
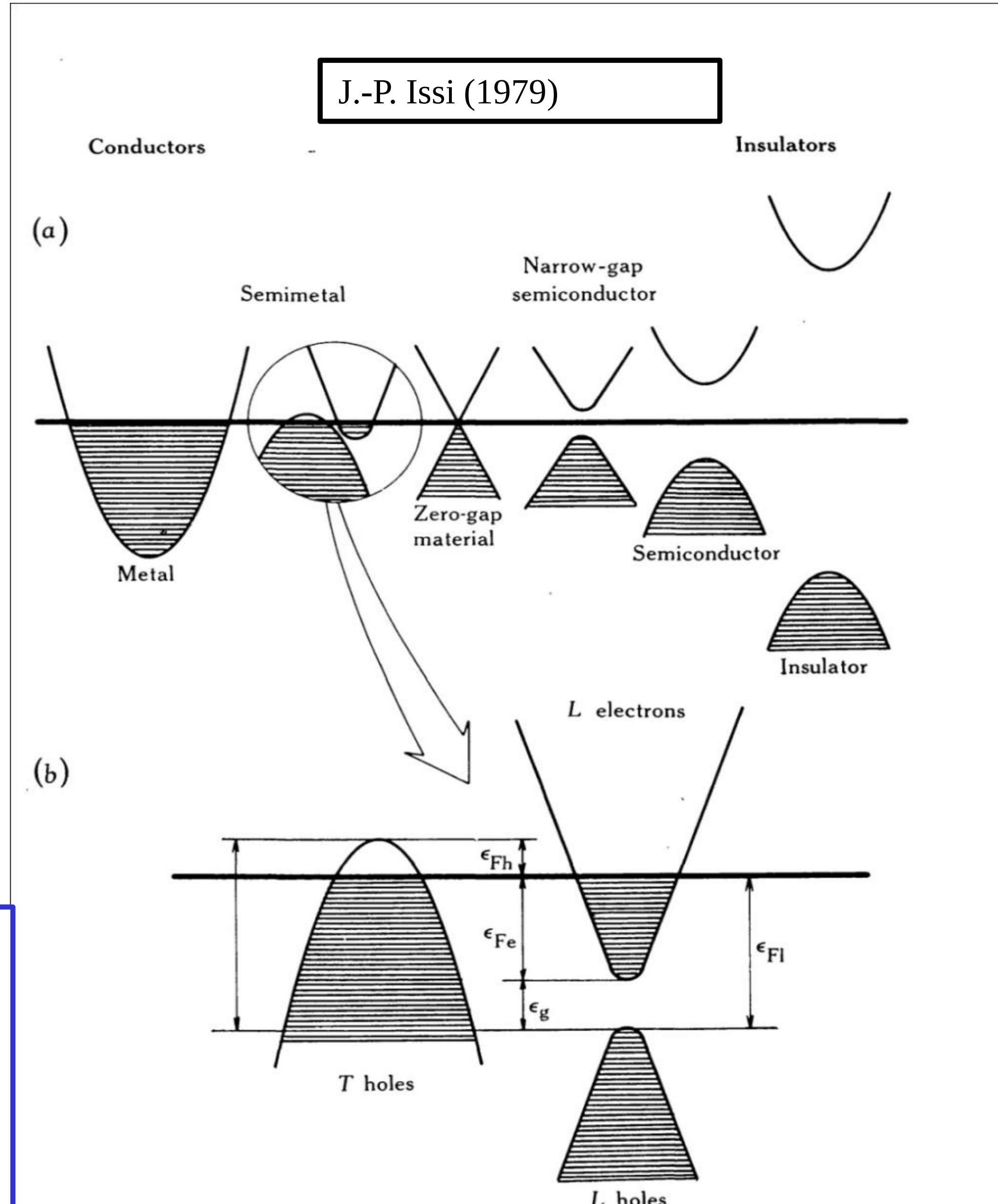
I. Introduction to bismuth

An old bulk semi-metal

(Ger. *Weisse Masse*, white mass; later Wisuth and Bisemutum) In early times bismuth was confused with **tin** and **lead**. Claude Geoffroy the Younger showed it to be distinct from lead in 1753.





Largest
- Diamagnetism
- Magnetoresistance
- Thermoelectric figure of merit

among elements at room temperature

Exceptional role in the history of condensed-matter physics

- **Seebeck effect (1821)**
- **Nernst effect (1886)**
- **Giant magnetoresistance [Kapitza] (1928)**
- **Shubnikov - de Haas effect (1930)**
- **de Haas - van Alphen effect (1930)**

- A small Fermi surface

[10^{-5} of the Brillouin zone] λ_F~ 10 - 70 nm

- A long mean-free-path

[l_e~ 2 μm at room temperature; quasi-balistic at T=0]

1964: The first irruption of Dirac Hamiltonian in condensed matter

J. Phys. Chem. Solids Pergamon Press 1964. Vol. 25, pp. 1057–1068. Printed in Great Britain.

MATRIX ELEMENTS AND SELECTION RULES FOR THE TWO-BAND MODEL OF BISMUTH

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(*Received* 7 *April* 1964)

Abstract—The two-band model of Cohen and Blount is used to investigate the wave functions and matrix elements for electrons in bismuth. After a suitable transformation the Hamiltonian takes the

We will commence our investigation by reviewing the two-band model, following closely the methods of COHEN and BLOUNT.[5] The resulting equations are essentially identical to those of the Dirac theory, and many of the methods employed there are useful in the present problem. In particular, the electron energy-momentum relation has the relativistic form:

$$E^2 = \left(\frac{E_G}{2}\right)^2 + E_G\left(\frac{p \cdot \overleftrightarrow{\alpha} \cdot p}{2}\right) \qquad (1)$$

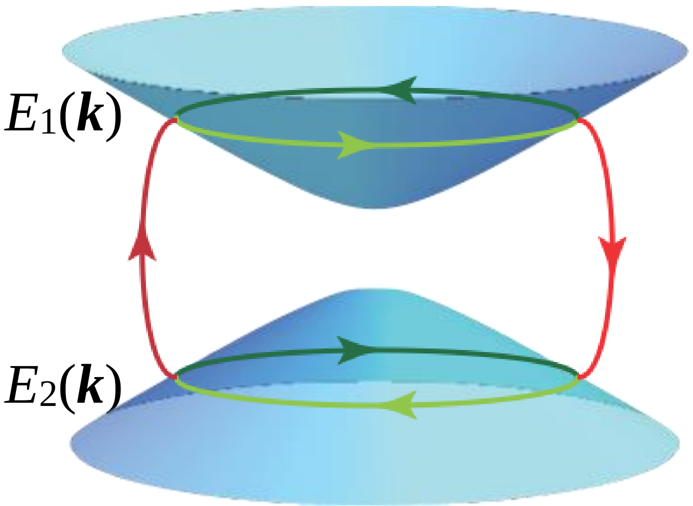
Magnetic susceptiblity

Material	Volume magnetic susceptoibility	
Units	SI	CGS (*emu*)
WATER	-9.035×10^{-6}	-7.190×10^{-7}
Bismuth	-1.66×10^{-4}	-1.32×10^{-5}
Diamond	-2.2×10^{-5}	-1.7×10^{-6}
Graphite (perpendicular to c-axis)	-1.4×10^{-5}	-1.1×10^{-6}
Graphite	-8.3×10^{-4}	-6.6×10^{-5}
He	-9.85×10^{-10}	-7.84×10^{-11}
Xe	-2.37×10^{-8}	-1.89×10^{-9}
O2	3.73×10^{-7}	2.97×10^{-8}
N2	-5.06×10^{-9}	-4.03×10^{-10}

Source: Wikipedia

Largest [average] diamagnetism among non-superconducting solids

The large diamagnetism can be traced to interband effects

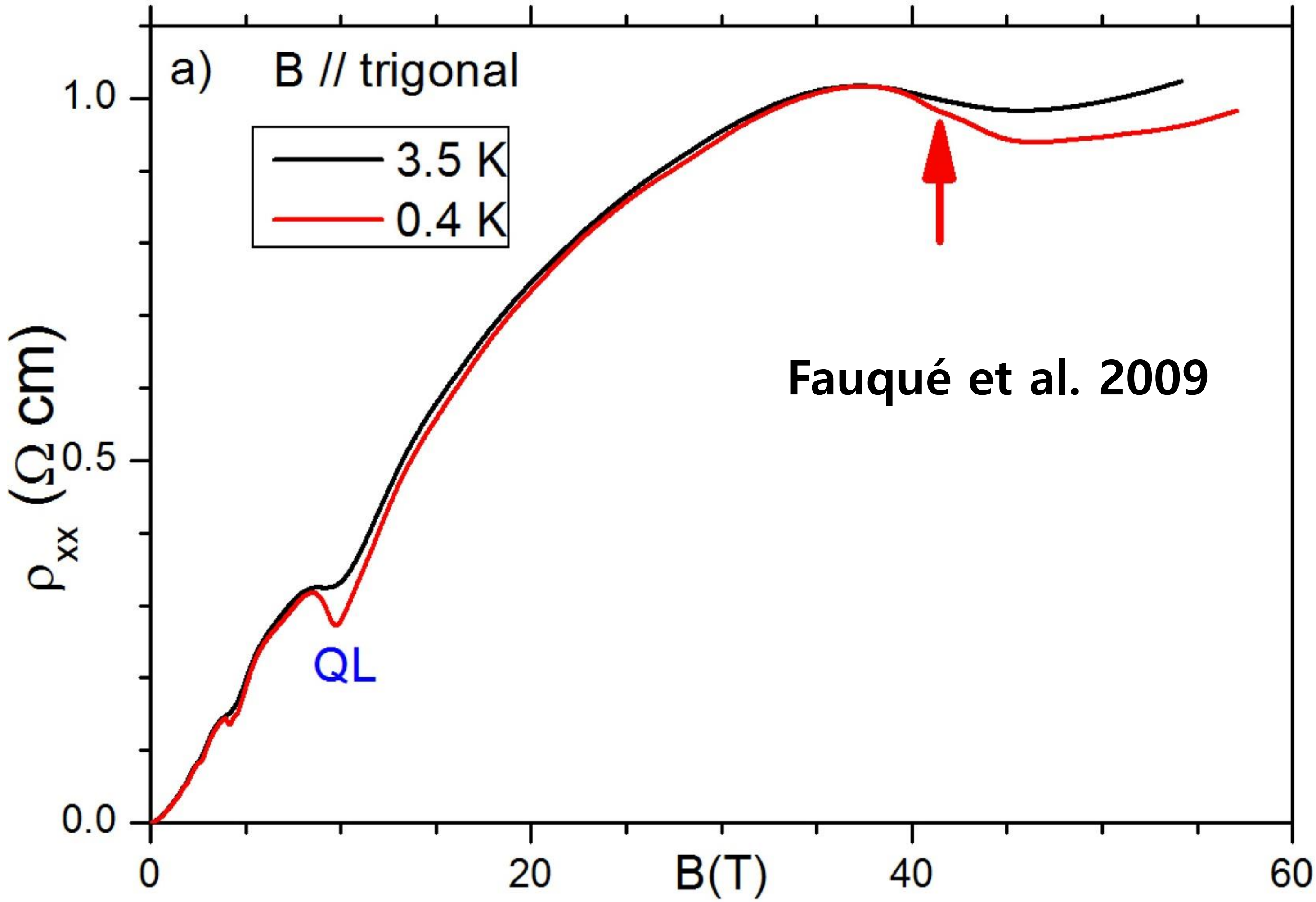


Beyond the Landau-Peierls formula for diamgnetism

$$\chi_{\mathrm{LP}} = \frac{e^2}{6\pi^3 c^2} \sum_{n,\boldsymbol{k}} \left\{ \frac{\partial^2 E_n}{\partial k_x^2} \frac{\partial^2 E_n}{\partial k_y^2} - \left(\frac{\partial^2 E_n}{\partial k_x \partial k_y} \right)^2 \right\} \frac{\partial f(E_n)}{\partial E_n}$$

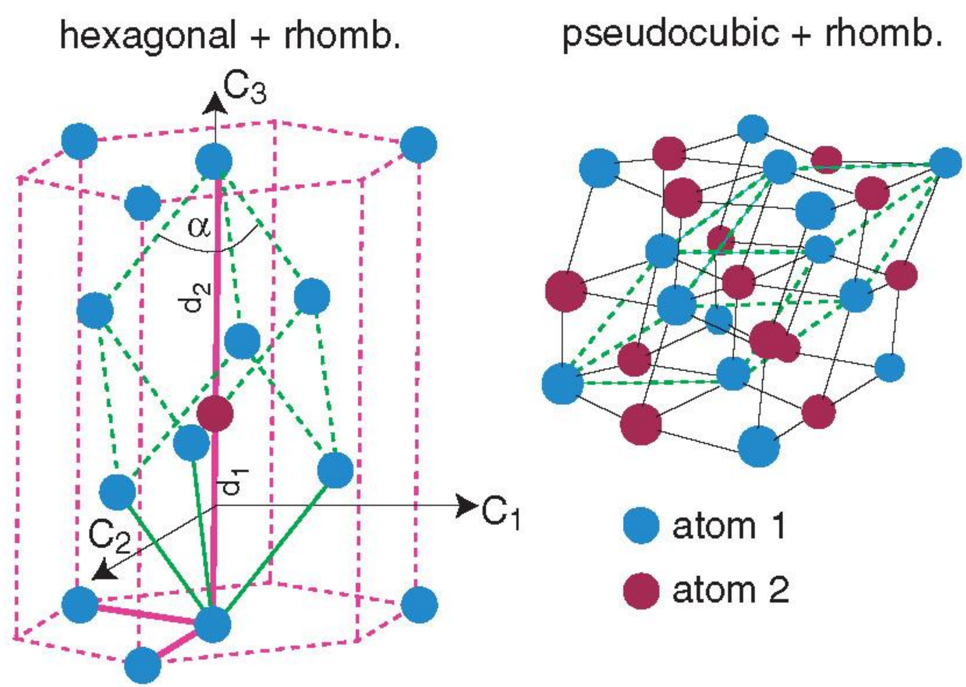
H. Fukuyama and R. Kubo, J. Phys. Soc. Japan 28, 570 (1970)

Largest magnetoresistance among solids



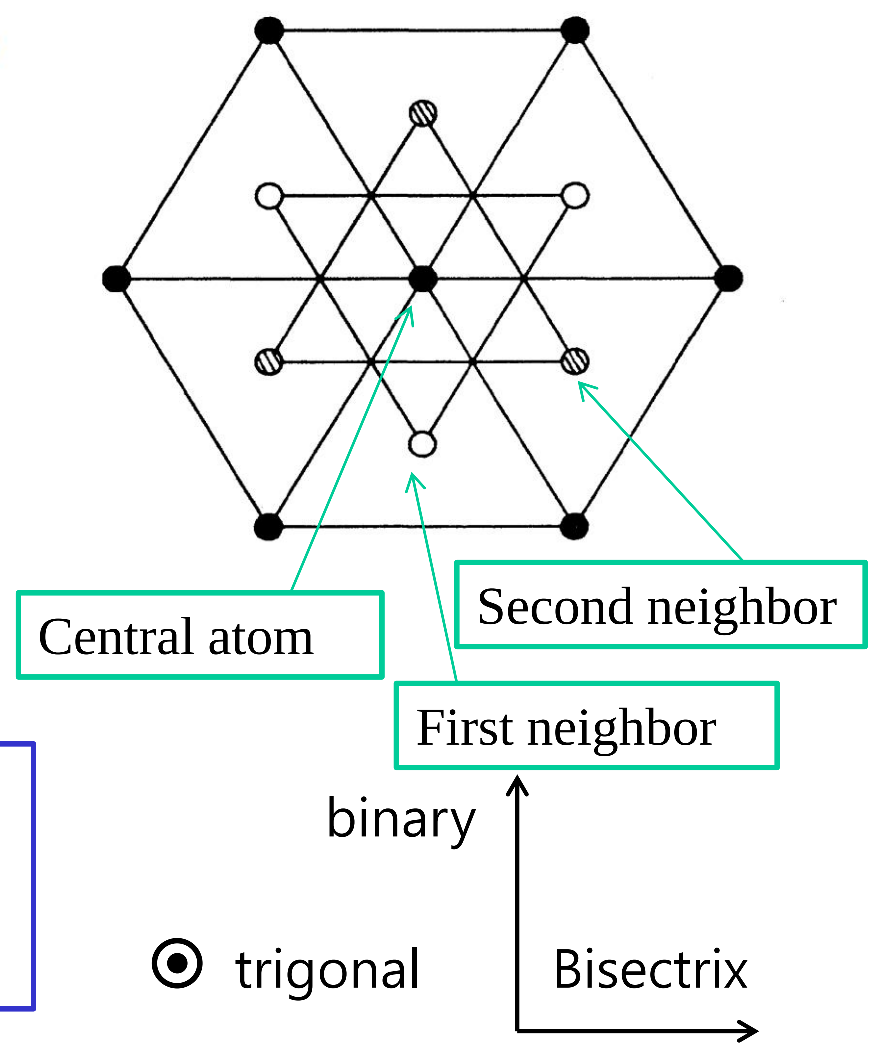
- A millionfold increase by 10 T
- Mobility as large as 10^8 $Vcm^{-1}s^{-1}$

The crystal structure



Hoffman, 2006

Liu & Allen 1995



“Evidently, no two- or three-body force law would make such a configuration stable.”
Rudolf Peierls, *More surprises in theoretical physics*

Electronic structure, phase stability, and semimetal-semiconductor transitions in Bi

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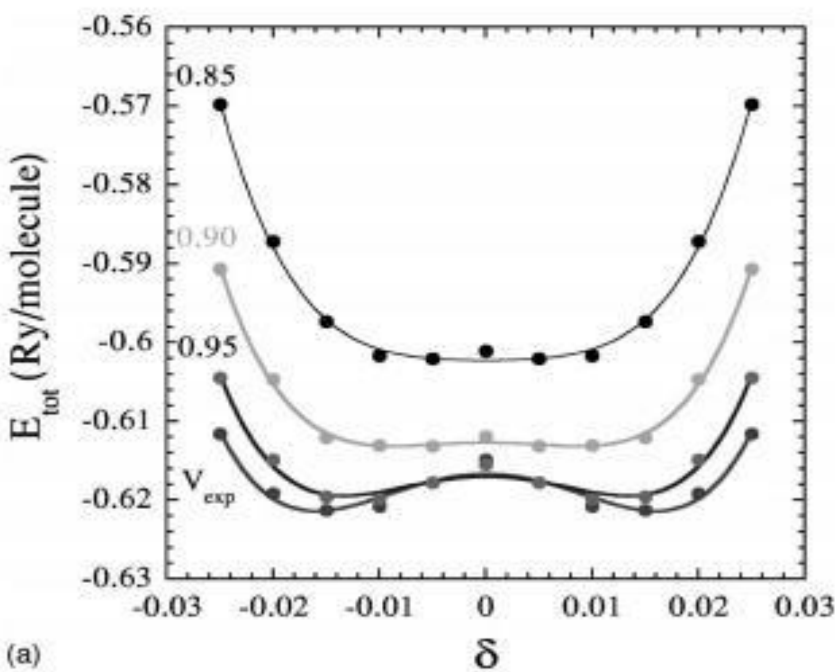
(Received 6 July 1999)

The structural stability of bulk Bi is studied using the local-density full-potential linear muffin-tin orbital method. The effect of both the trigonal shear angle and internal displacement on the electronic structure is determined. It is shown that the internal displacement changes the Bi electronic structure from a metal to a semimetal, in qualitative agreement with a Jones-Peierls-type transition. The total energy is calculated to have ... rigonal phase. We ... to a semimetal- ... onstant mismatch, ... trol their thermo-

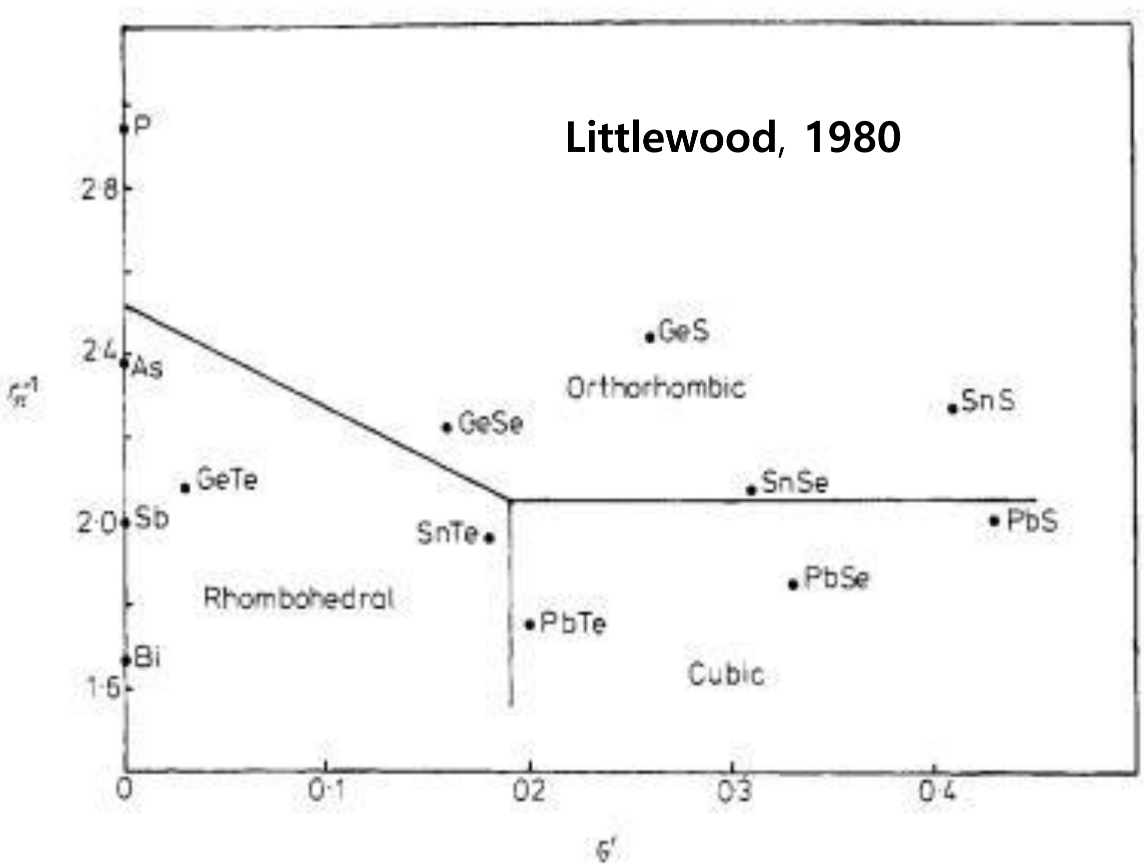


(a)

In agreement with experimentally-observed cubic structure under pressure

Sharing 5 electrons lead to complications!

The crystal structure of IV–VI compounds: I



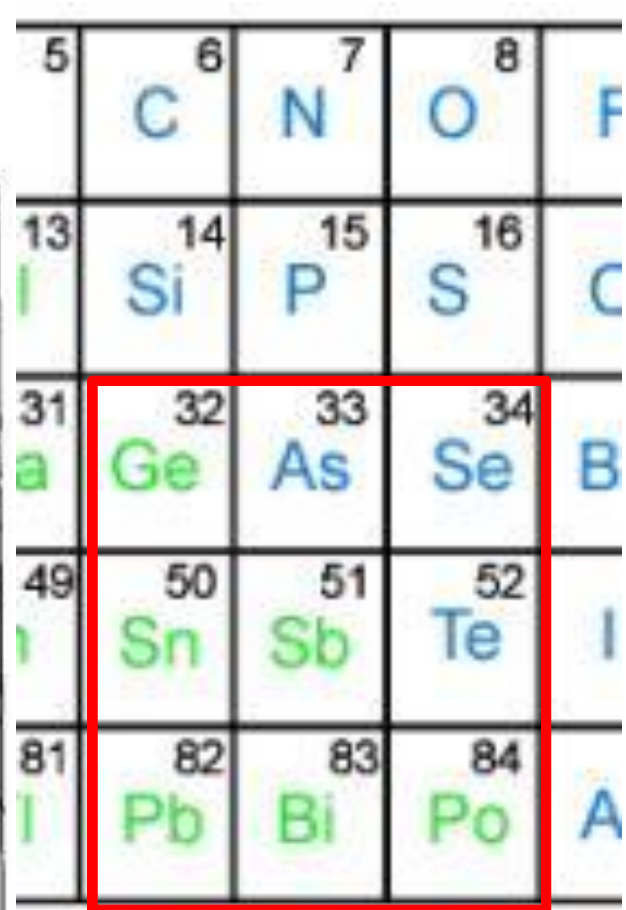
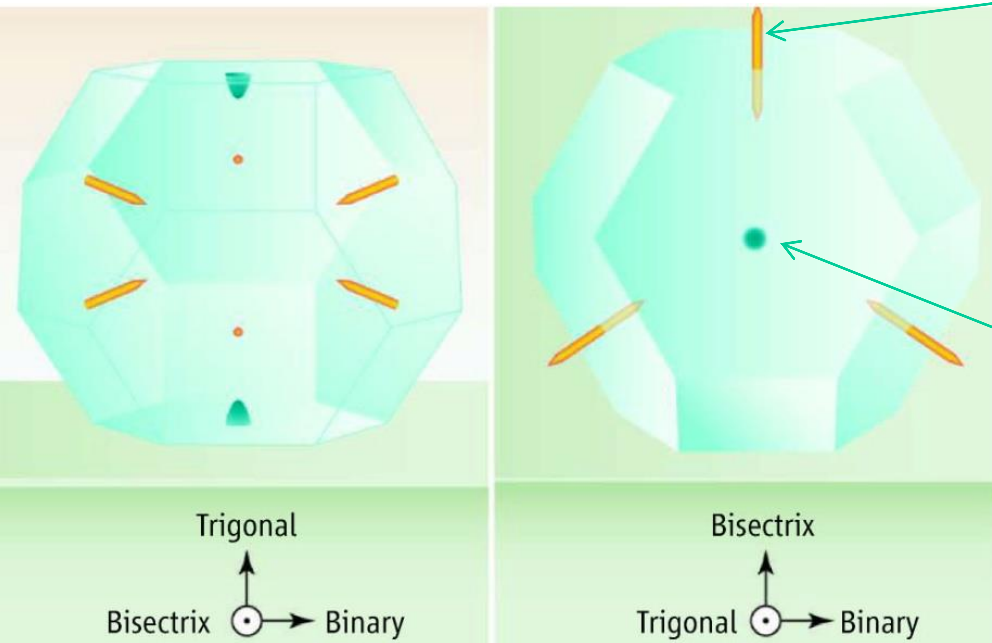


Figure 1. St John–Bloch plot for the IV–VI compounds and group V elements, using the bond orbital coordinates r'_σ and r_π^{-1} (equations (1.3) and (1.5)), calculated from the orbital radii of Chelikowsky and Phillips (1978). Increasing ionicity is measured by r'_σ, and increasing covalency by r_π^{-1}.

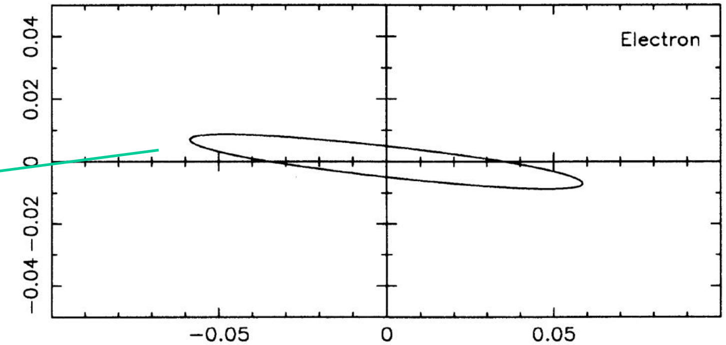
II. Angle-resolved Landau spectrum

- **A complex spectrum near the quantum limit**
- **The g-factor and the Zeman-to-cyclotron-energy ratio**

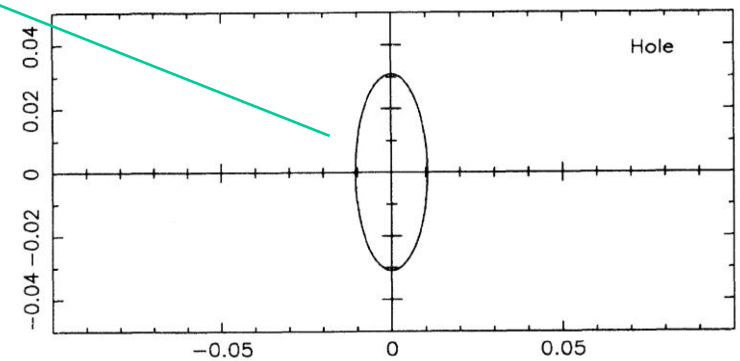
The Fermi surface



Liu & Allen, PRB 1995

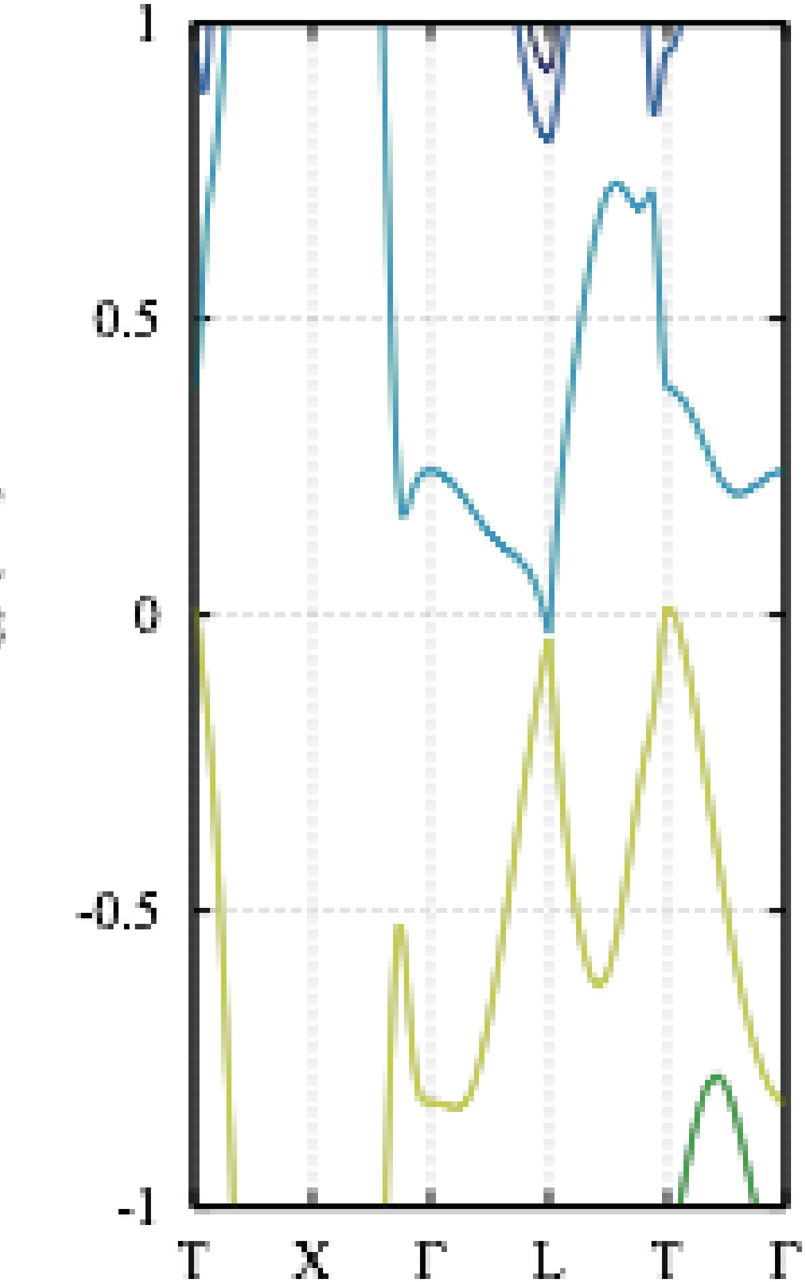


Electron
Non-Parabolic
Mass anisotropy 200
E_F= 27 meV

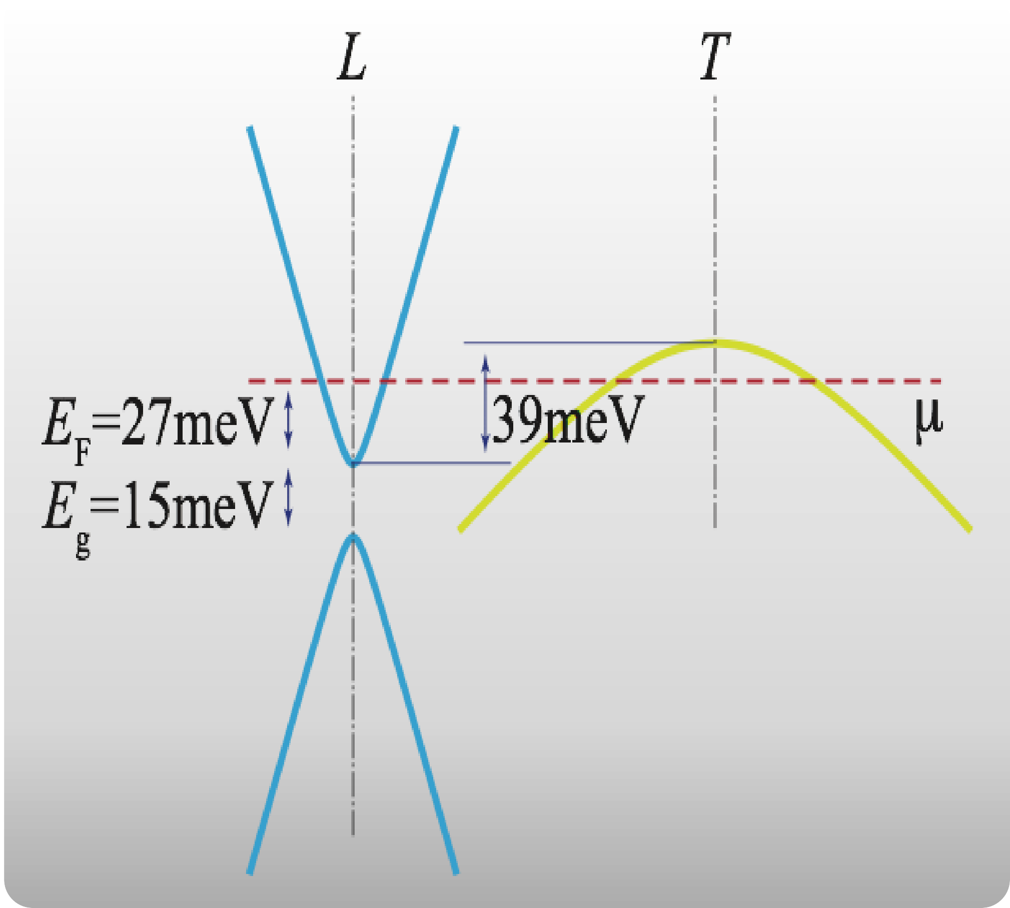


Hole
Parabolic
Mass anisotropy 10
E_F= 15 meV

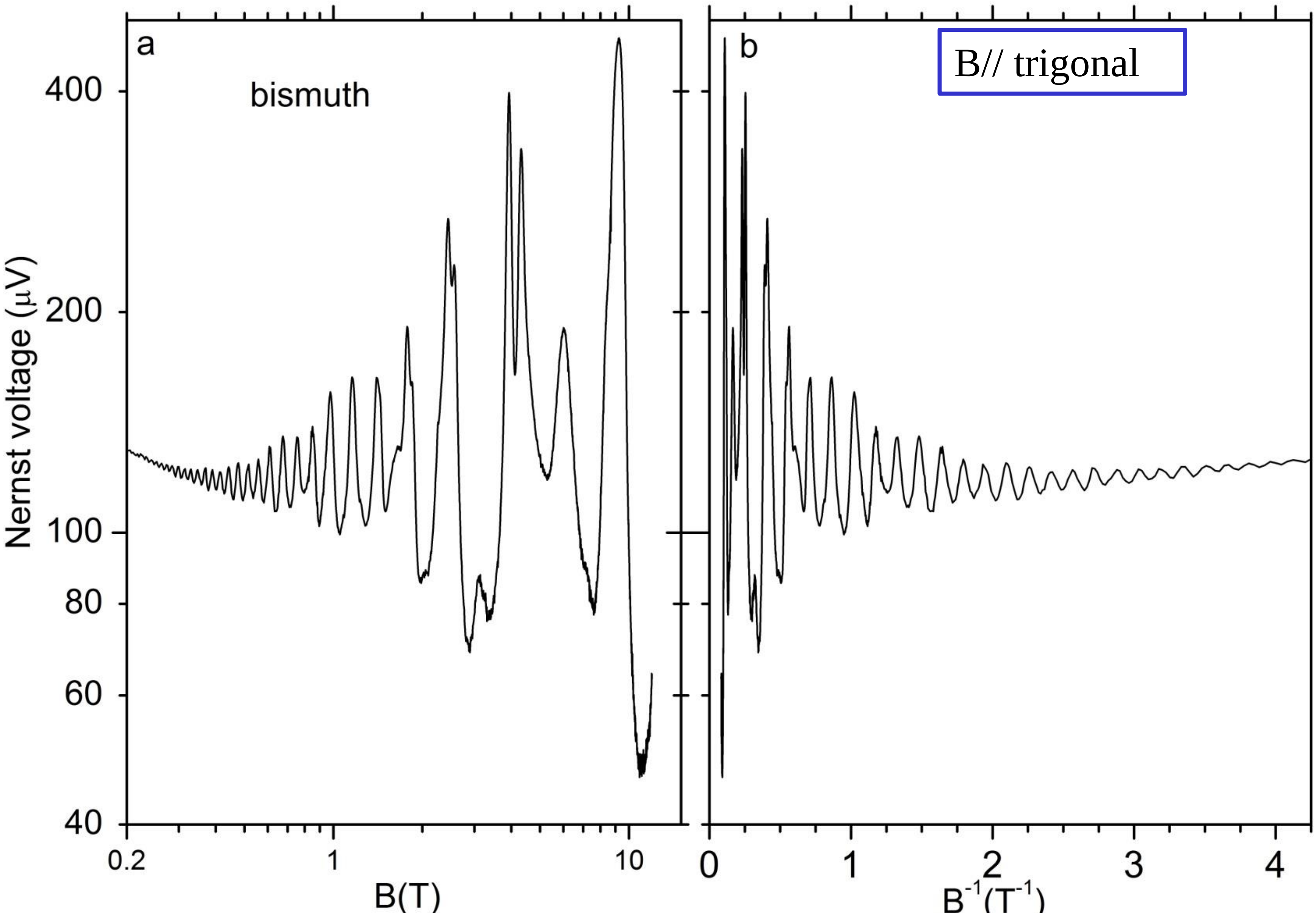
Theses pockets occupy 10^{-5} of the Brillouin zone!



Fuseya 2015

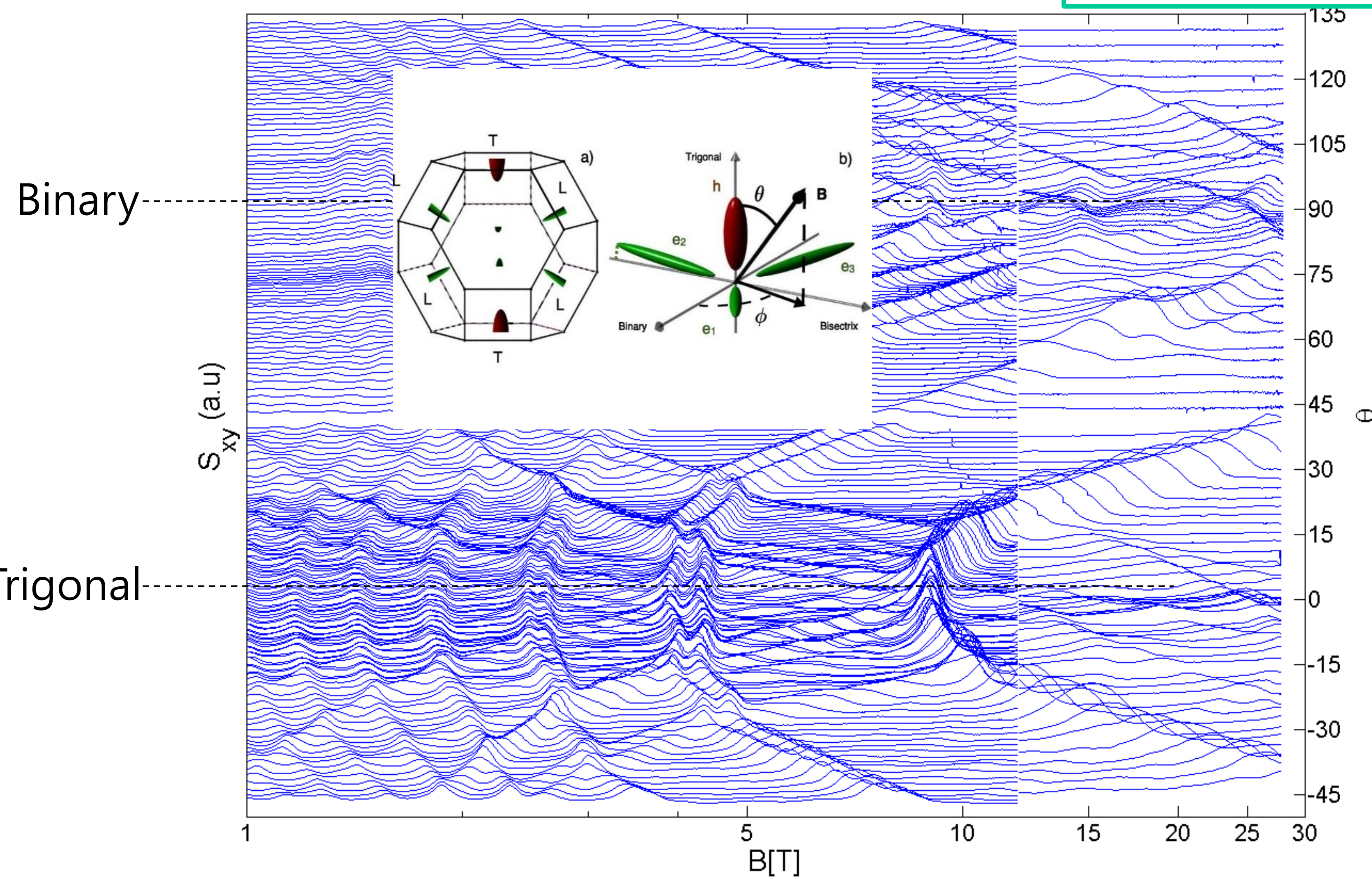


Giant quantum oscillations of the Nernst response



Angle-resolved Nernst signal for a rotating magnetic field

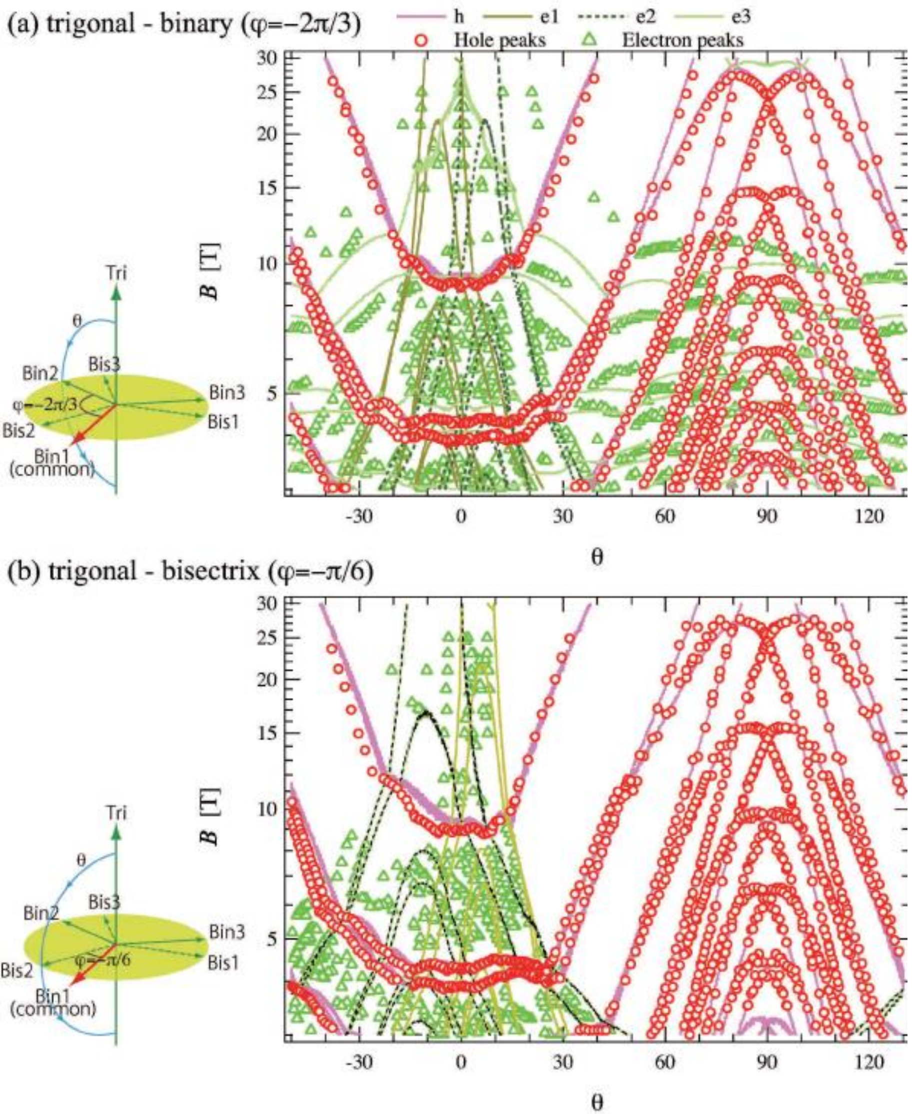
Zhu et al. PNAS (2012)

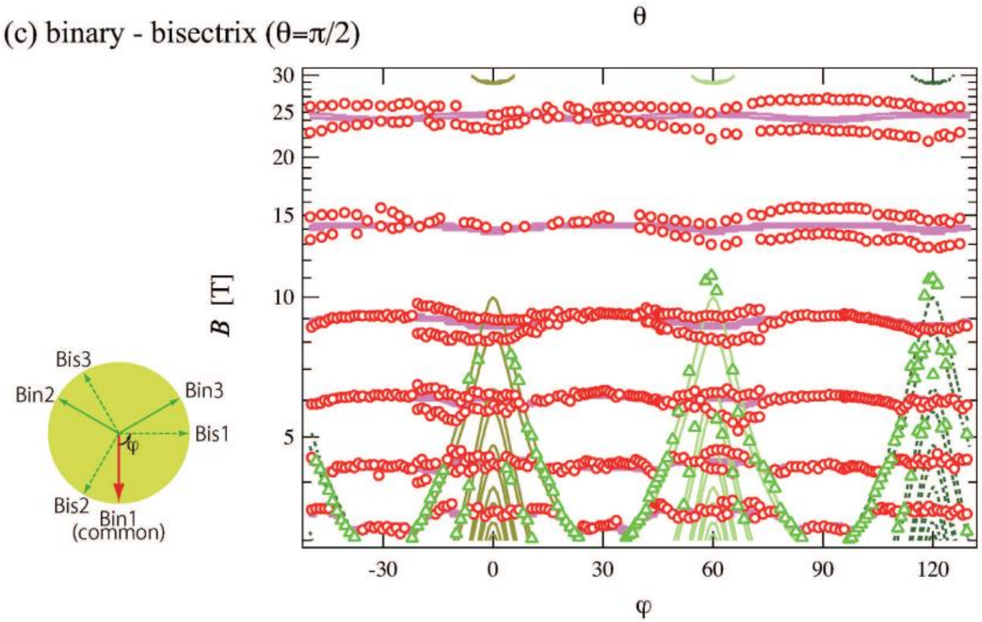


0.49K, 12T

T=1.5K,12T- 28T

Landau spectrum (experiment and theory)

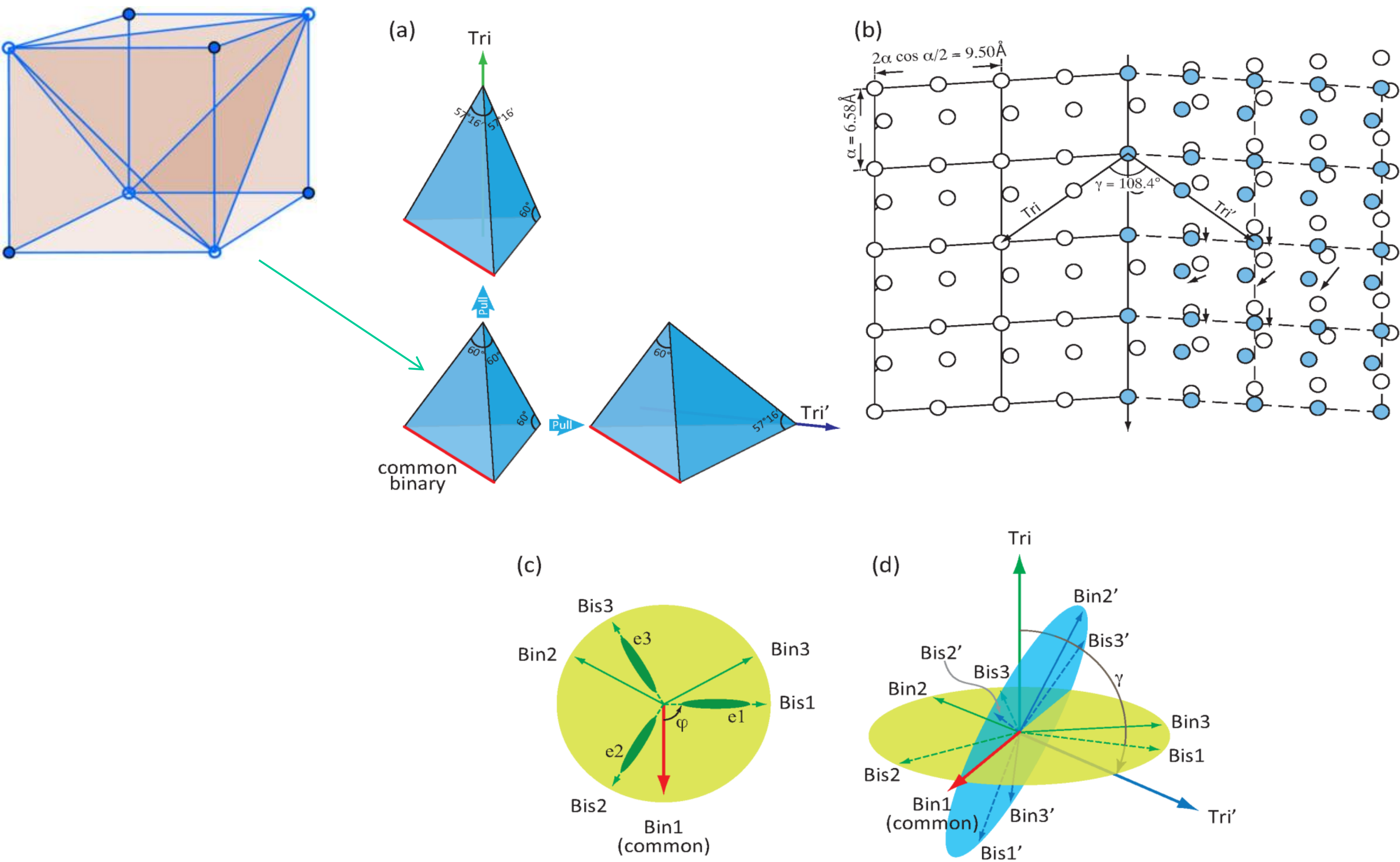




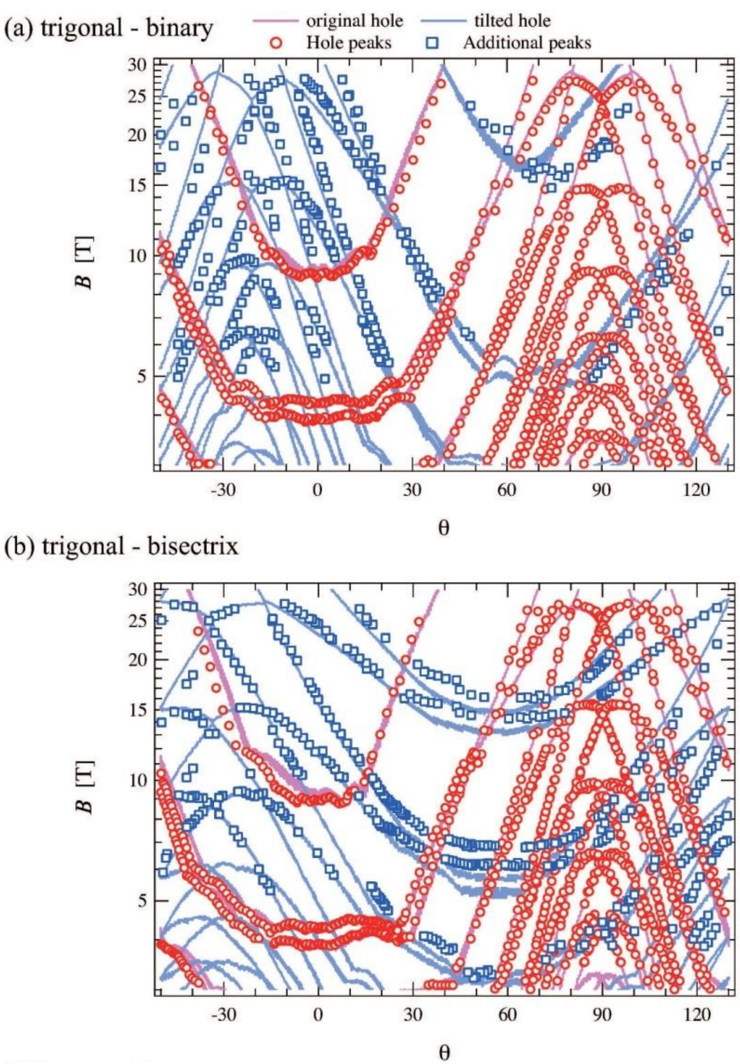
Symbols: experimental data
Red: hole
Green: electron
Lines: theory

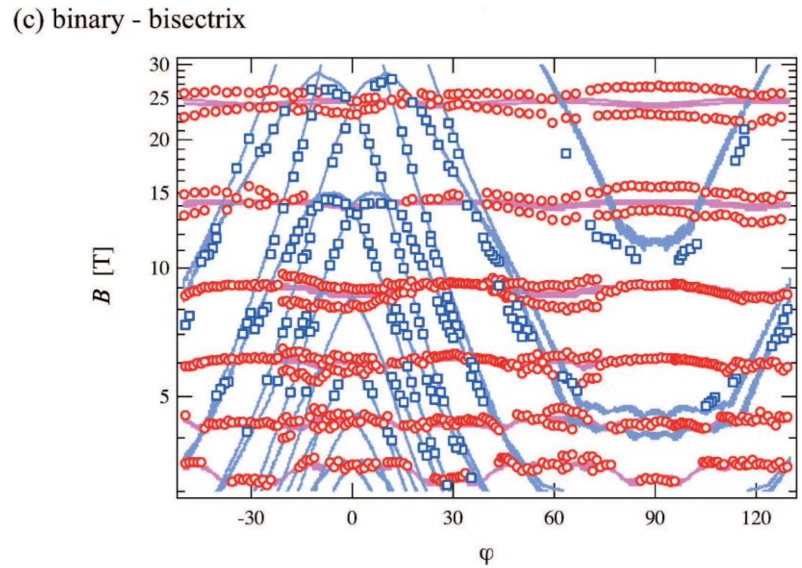
Zhu et al. PNAS (2012)

Twinning in bismuth



Single-particle theory explains additional peaks





Red lines and open circles: theory and experiment for holes

Blue lines and open squares: experimental additional peaks and theory for a tilted crystal

Electrons and holes in bismuth

Model

Hole: Smith-Baraff-Rowell (SBR) model

$$E = E_0 - \left[\left(n + \frac{1}{2}\right)\hbar\omega_c + \frac{p_H^2}{2m_H} \pm \frac{1}{2} g\beta_0 H\right]$$

Electrons: Vecchi-Pereira-Dresselhaus (VPD) model

$$j = (n + ½ + s) > 0$$

$$E = -\frac{E_g}{2} \pm \left[\frac{1}{2}\sqrt{E_g^2 + 4E_g\left(j\beta_B H + \frac{p_H^2}{2m_H}\right)} - 2s|G\beta|H\right]$$

Parameters

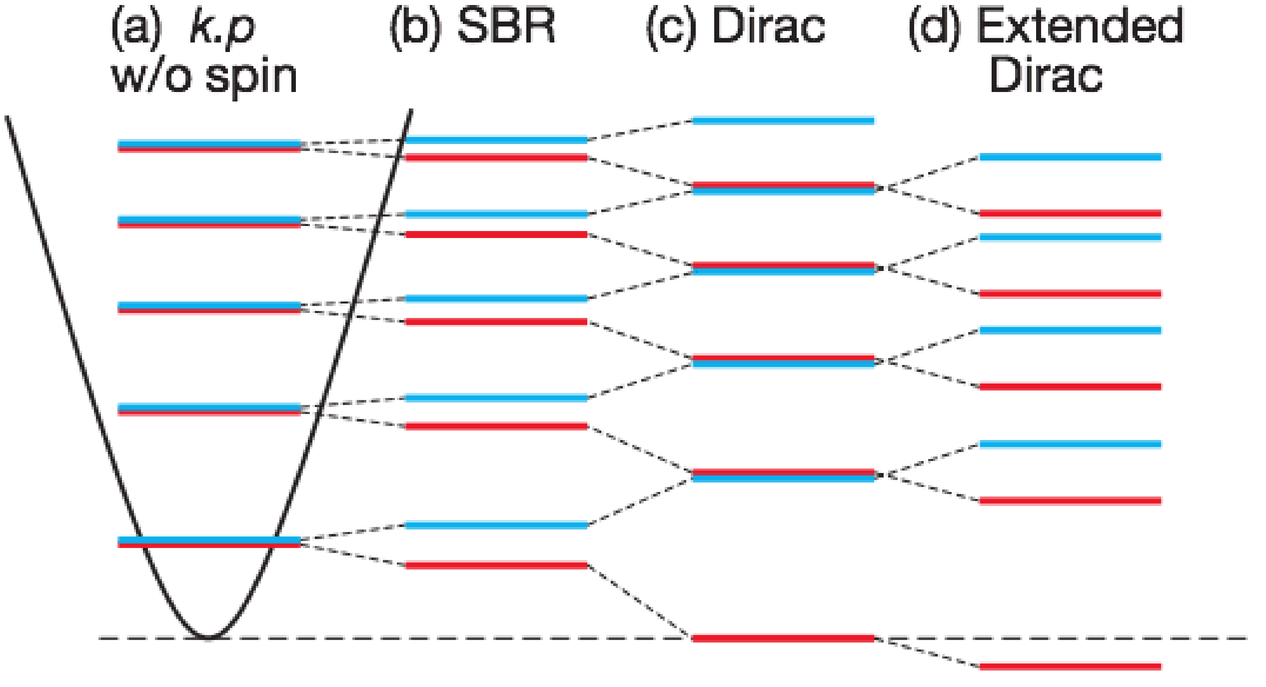
	$B \parallel$ Binary	$B \parallel$ Bisectrix	$B \parallel$ Trigonal
m_c^{e2}	0.0272	0.00189	0.0125
$m_c^{e1,e3}$	0.00218	0.00375	0.0125
m_z^{e2}	0.00124	0.257	0.00585
$m_z^{e1,e3}$	0.193	0.0653	0.00585
g^{e2}	73.5	1060	159
$g^{e1,e3}$	917	533	159
g'^{e2}	−7.26	24.0	−7.92
$g'^{e1,e3}$	16.2	0.545	−7.92
$1 + (m_c g')^{e2}/2$	0.90	1.02	0.950
$1 + (m_c g')^{e1,e3}/2$	1.01	1.00	0.950
M_c	0.221	0.221	0.0678
M_z	0.0678	0.0678	0.721
G	0.791	0.791	62.6
$E_Z/\hbar\omega_c$	0.0875	0.0875	2.12

Light and anisotropic electrons

Large g-factors

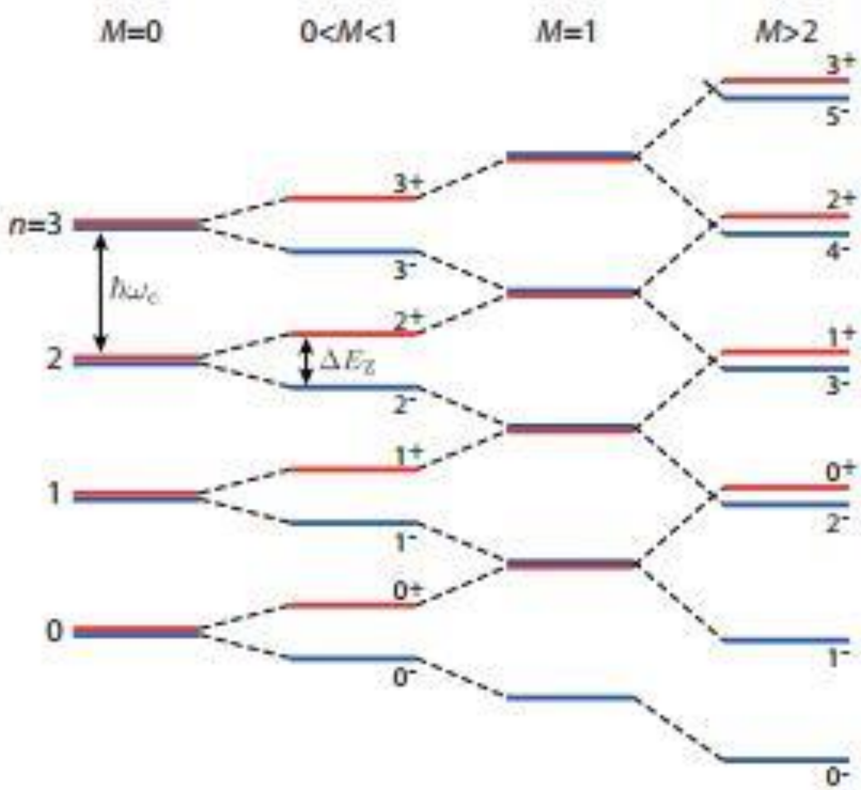
Heavier and less anisotropic holes

Zeeman and cyclotron energies



- In the case of electrons, Dirac-like spectrum with a small and anisotropic correction.
- The gfactor is large because electrons are light.

Zeeman and cyclotron energies

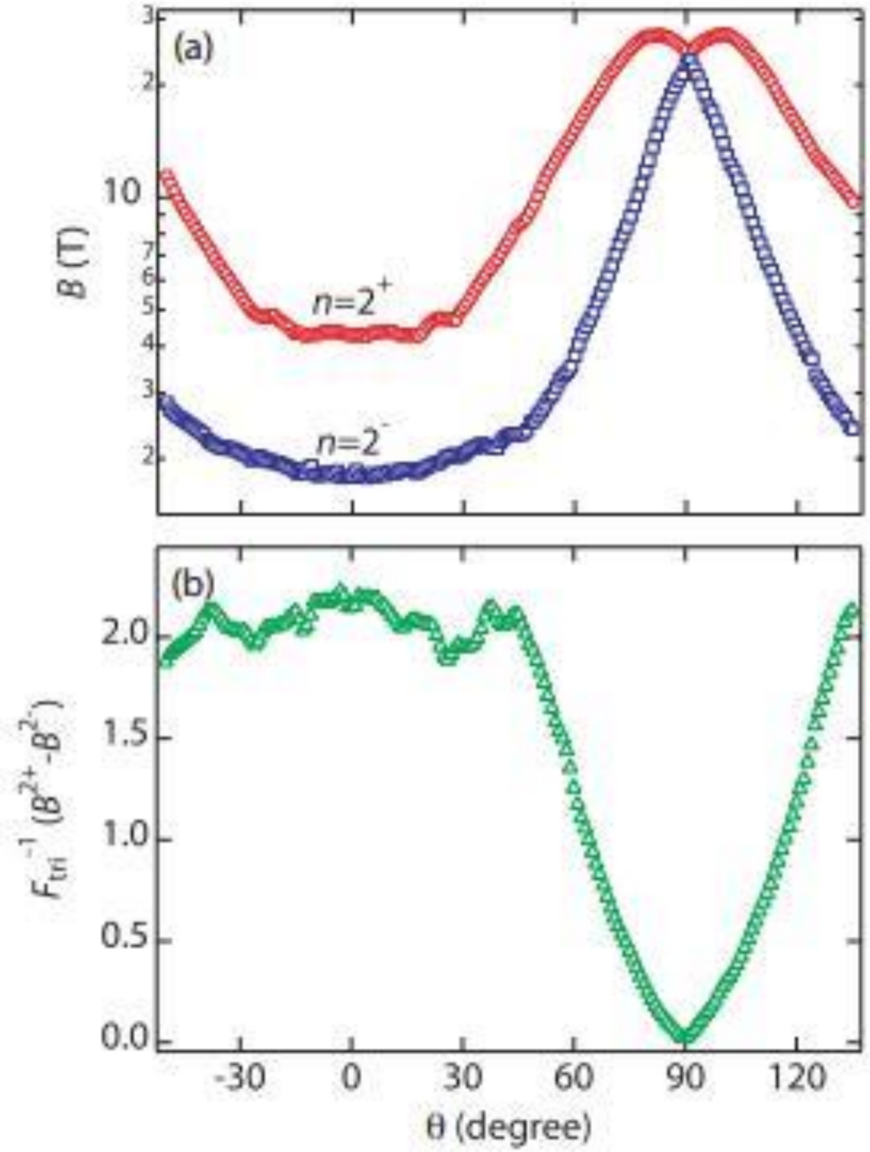


$$M = \frac{\Delta E_Z}{\hbar \omega_c}$$

	Graphite		InSb	Bi	
position	K (ele.)	H (hole)	Γ	L (ele.)	T (hole)
m_c/m	0.038	0.057	0.014	0.0019-0.027	0.068-0.22
$\bar{g}$	2.5	2.5	52	74-1060	0.79-63
$M = m_c\bar{g}/2m$	0.048	0.073	0.36	0.9-1.0	0.0-2.12
atomic SO (eV)	0.005	0.005	0.27, 0.68	1.8	1.8

Holes in bismuth stand out!

Zeeman and cyclotron energies



$$M = \frac{\Delta E_Z}{\hbar \omega_c}$$

The ratio of Zeeman to cyclotron energy for holes:

i) is larger than 2 when the field is parallel to the trigonal axis

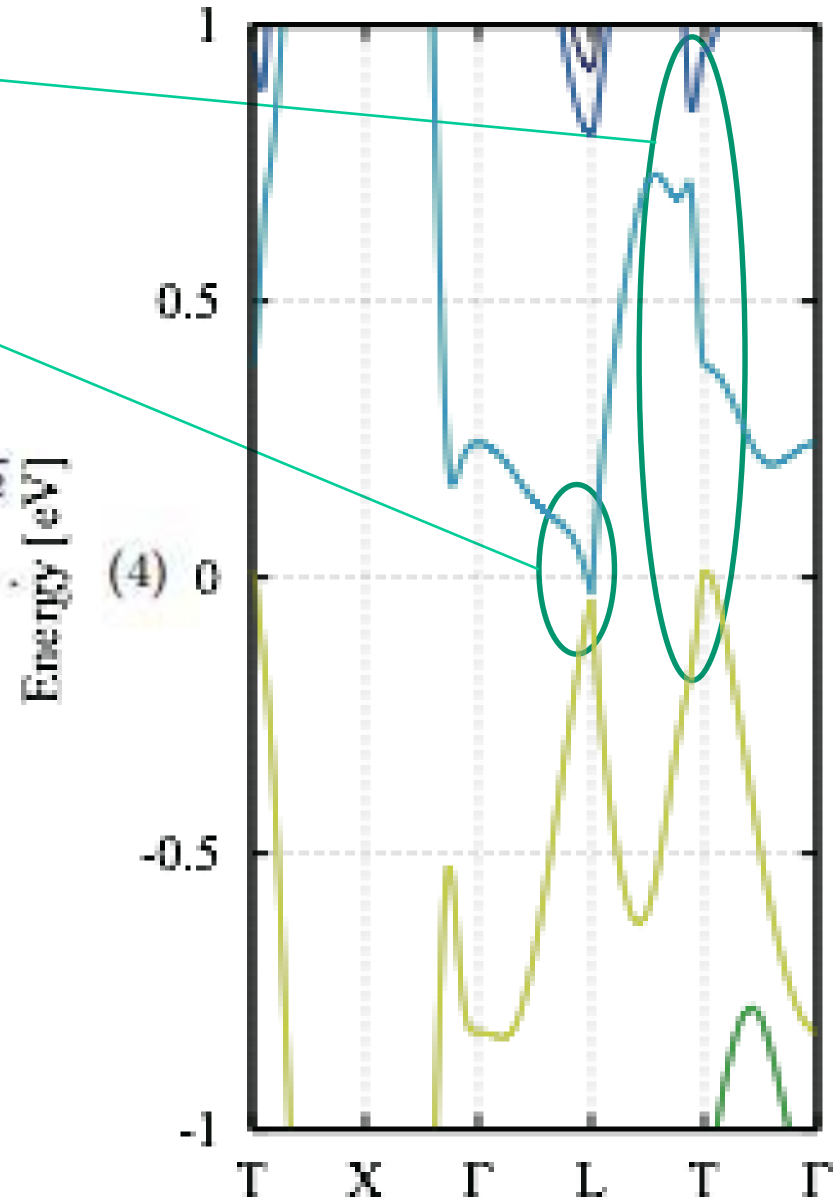
ii) becomes vanishingly small for the perpendicular orientation?

Zeeman and cyclotron energies

For holes one needs to consider at least three bands! $M > 2$

For electrons the two-band model is good enough! $M \sim 1$

$$M = \sqrt{\left|\sum_{n\neq 0} \frac{a_n^2}{E_0 - E_n}\right|^2 \bigg/ \left(\sum_{n\neq 0} \frac{|a_n|^2}{E_0 - E_n}\right)^2}. \quad (4)$$

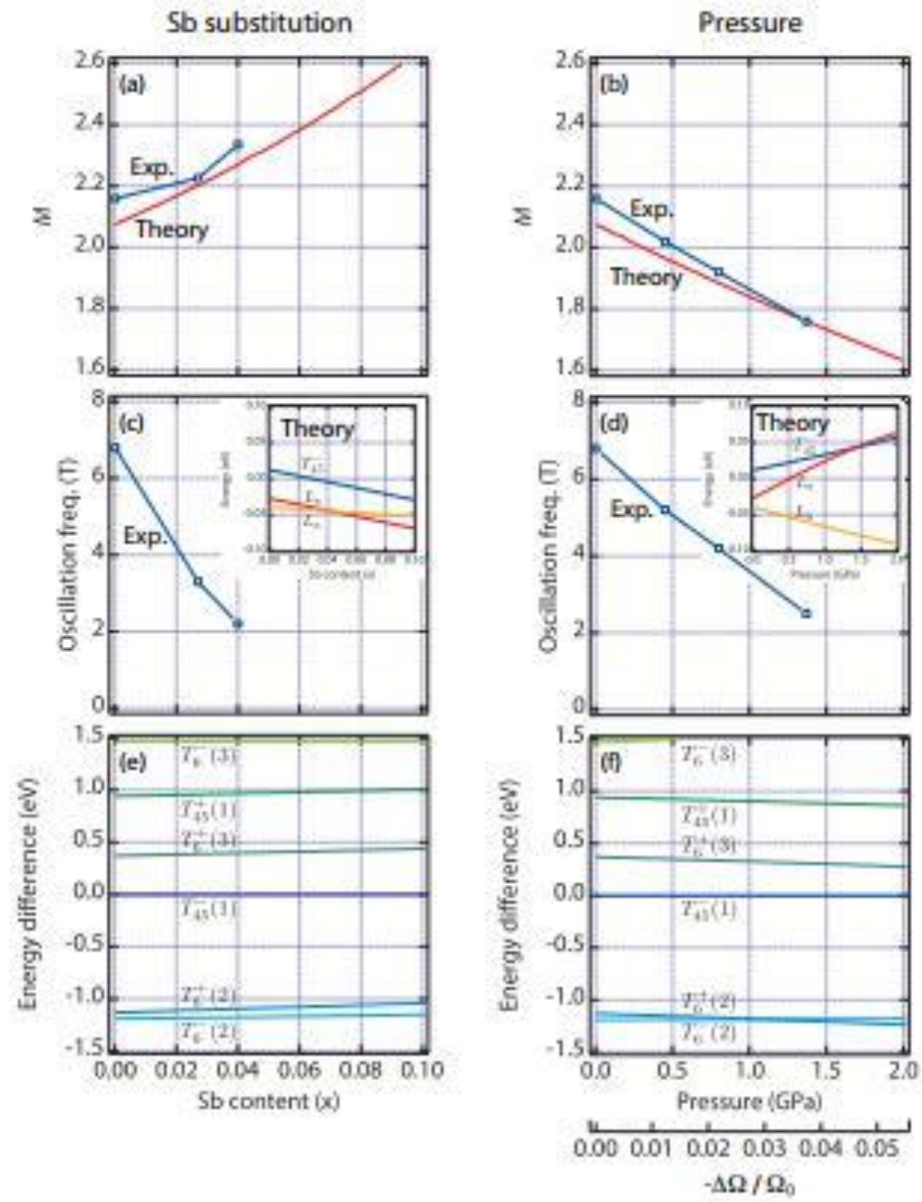


Y. Fuseya, ArXiv :1507.05996

Multiband k.p theory

- Provides an explanation for the magnitude and anisotropy of M for holes at T-point.
- Explains its evoluion with pressure and Sb doping.
- Relevant to other cases of strong SOC like Bi_2Se_3, PbTe,…

Y. Fuseya, ArXiv :1507.05996



III. The valley degree of freedom

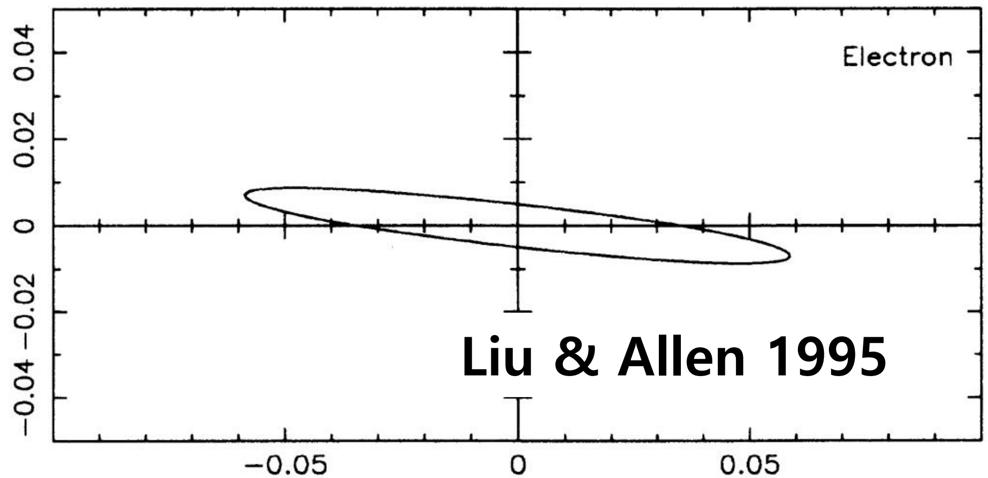
- **SEMI-CLASSIC HIGH-FIELD TRANSPORT**
- **SPONTANEOUS LOSS OF THREEFOLD SYMMETRY**
- **VALLEY NEMATICITY?**

Anisotropic Dirac valleys in bismuth

	B// binary	B// bisectrix	B// trigonal
m (e)	0.0012	0.26	0.0058

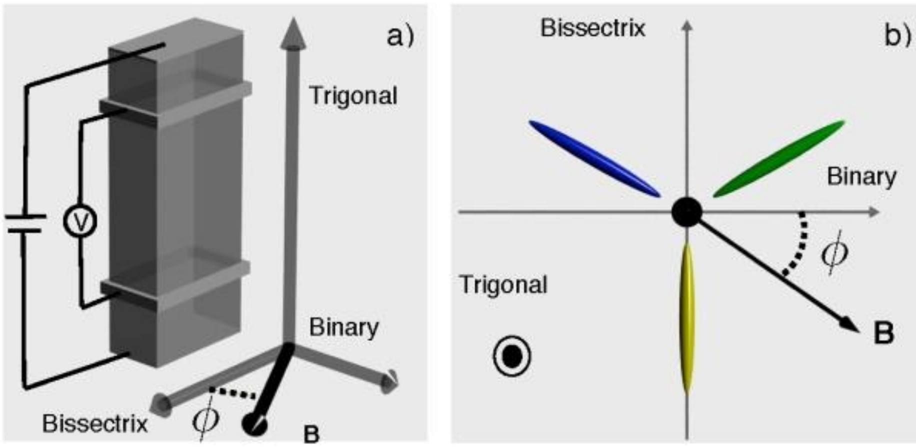
The anisotropy of the electron mass exceeds 200 !

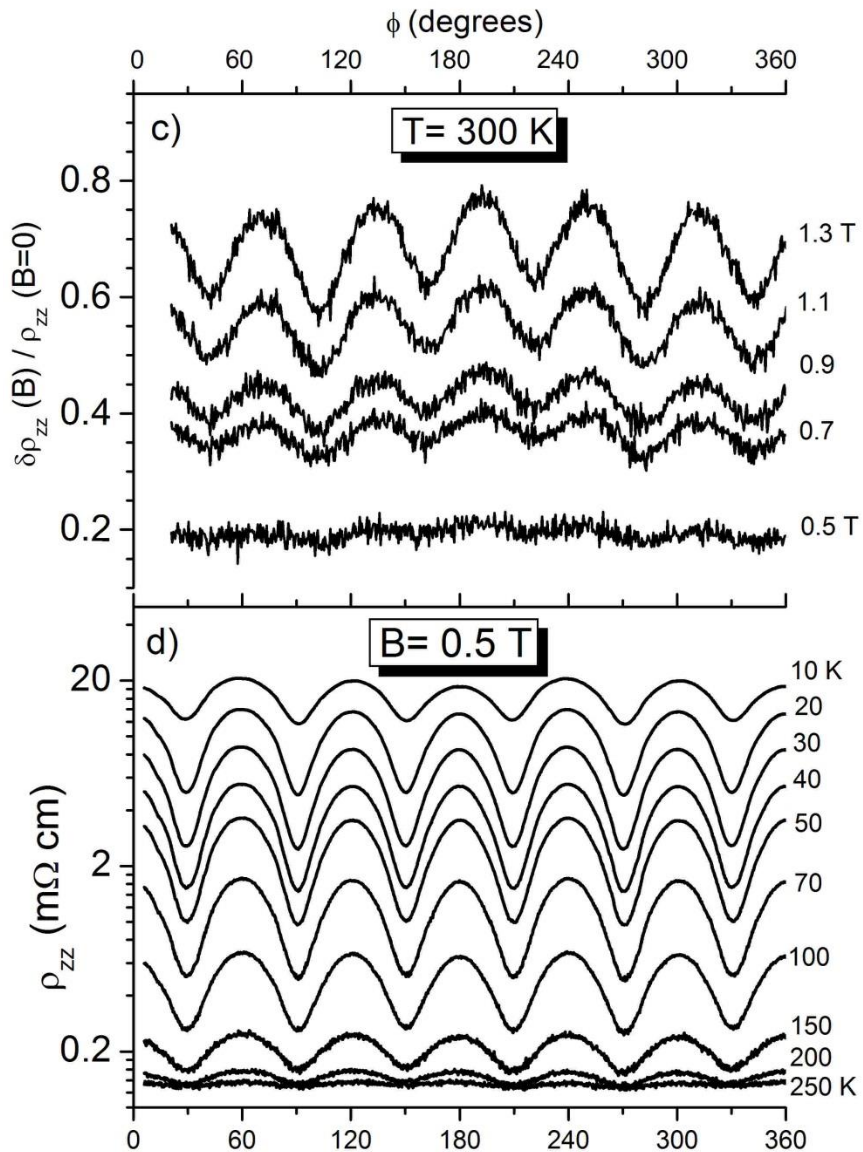
Wave-vector anisotropy: 14



Liu & Allen 1995

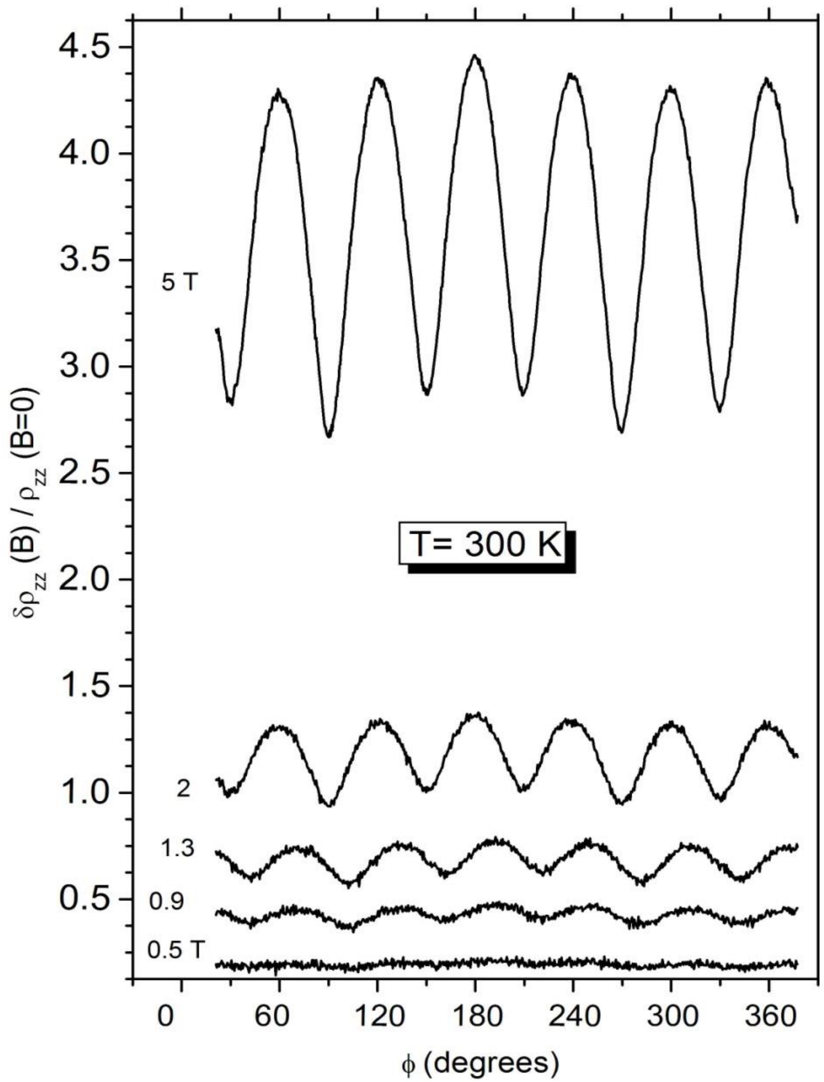
Angle-dependent Magnetoresistance

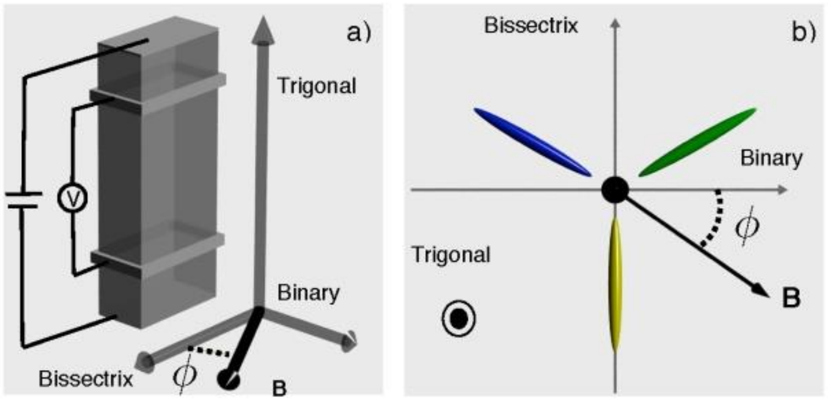




Mobility is largest when B // bisectrix
Therefore orbital magnetoresistance is largest!

Room-temperature oscillations





No other solid known to combine anisotropy and lightness:

- Mobility (10000 @300 K)
- Anisotropy (m_{bin}/m_{bis} > 200
- Lightness ($m \sim 10^{-3}\ m_e$)

UNIQUE TO BISMUTH!

Semi-classic transport theory

Boltzmann equation:
$$\mathbf{j} = \boldsymbol{\sigma}_0.(\mathbf{E} + \frac{1}{ne}\mathbf{j} \wedge \boldsymbol{B})$$
$$\boldsymbol{\sigma}_0 = ne\boldsymbol{\mu}$$

Abeles and Meiboom (1956)

When B≠ 0 $\mathbf{j} = \boldsymbol{\sigma}(\boldsymbol{B}).\mathbf{E}$ $\boldsymbol{\sigma}(\boldsymbol{B}) = ne(\boldsymbol{\mu}^{-1} + \mathbf{B})^{-1}$ *Aubrey (1971)*

σ, μ and B are tensors!

$$\mu = \begin{pmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_2 & 0 \\ 0 & 0 & \mu_3 \end{pmatrix} \quad B = \begin{pmatrix} 0 & -B_3 & B_2 \\ B_3 & 0 & -B_1 \\ -B_2 & B_1 & 0 \end{pmatrix}$$

If μ were a scalar, this would yield the familiar:

$$\sigma = \begin{pmatrix} \frac{ne\mu}{1+\mu^2 B^2} & \frac{ne\mu^2 B^2}{1+\mu^2 B^2} & 0 \\ \frac{-ne\mu^2 B^2}{1+\mu^2 B^2} & \frac{ne\mu}{1+\mu^2 B^2} & 0 \\ 0 & 0 & ne\mu \end{pmatrix}$$

Multi-valley bismuth

$$\boldsymbol{\sigma}_{total} = \sum_i \boldsymbol{\sigma}_e^i + \boldsymbol{\sigma}_h$$

Mobility tensor for the three electron pockets:

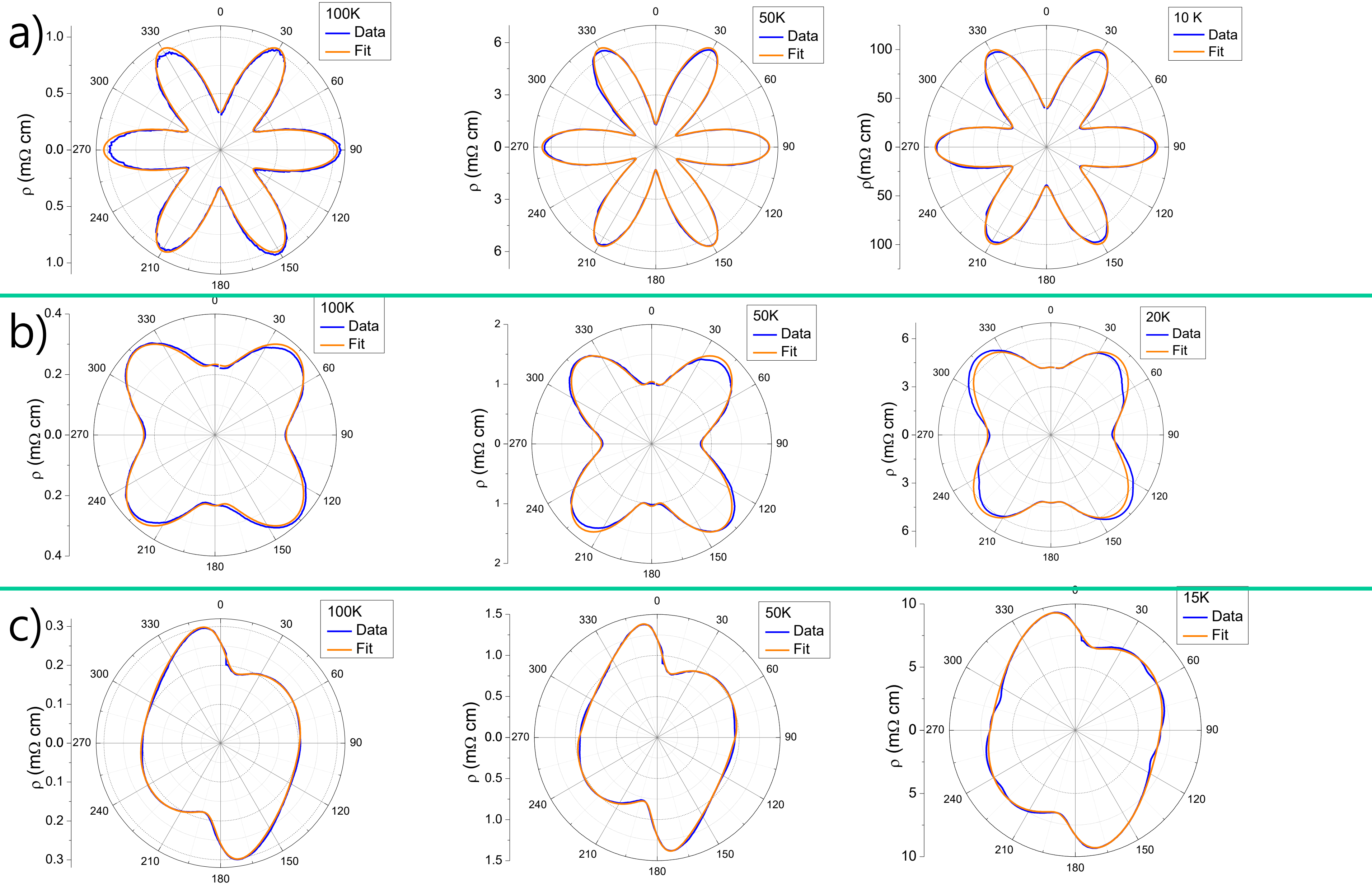
$$\hat{\mu}_a = \begin{pmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_2 & \mu_4 \\ 0 & \mu_4 & \mu_3 \end{pmatrix} \quad ; \quad \hat{\mu}_b = \hat{R}^{-1}_{2\pi/3} \cdot \hat{\mu}_a \cdot \hat{R}_{2\pi/3} \quad ; \quad \hat{\mu}_c = \hat{R}^{-1}_{4\pi/3} \cdot \hat{\mu}_a \cdot \hat{R}_{4\pi/3}$$

The rotation matrix

$$R^{\theta} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

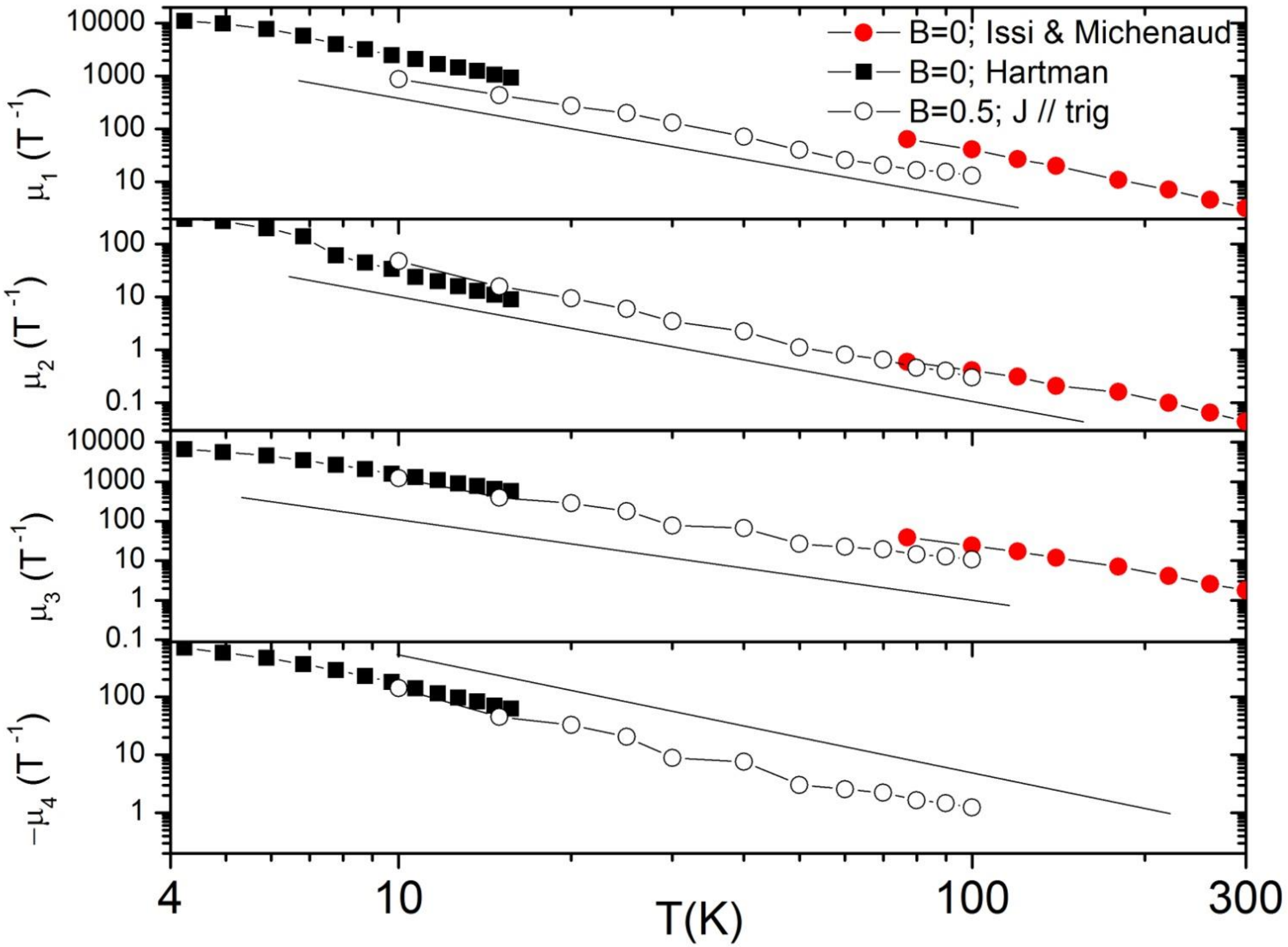
Mobility tensor for the hole-like pocket:

$$\nu = \begin{pmatrix} \nu_1 & 0 & 0 \\ 0 & \nu_1 & 0 \\ 0 & 0 & \nu_3 \end{pmatrix}$$



Theoretical fits and experimental data

Components of the mobility tensor of the Dirac electrons in bismuth

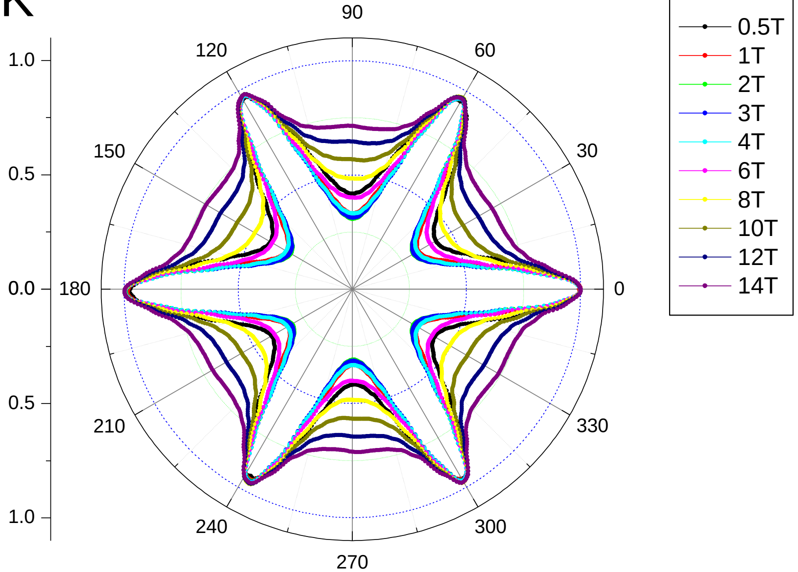


- T^{-2} behavior
- e-e scattering

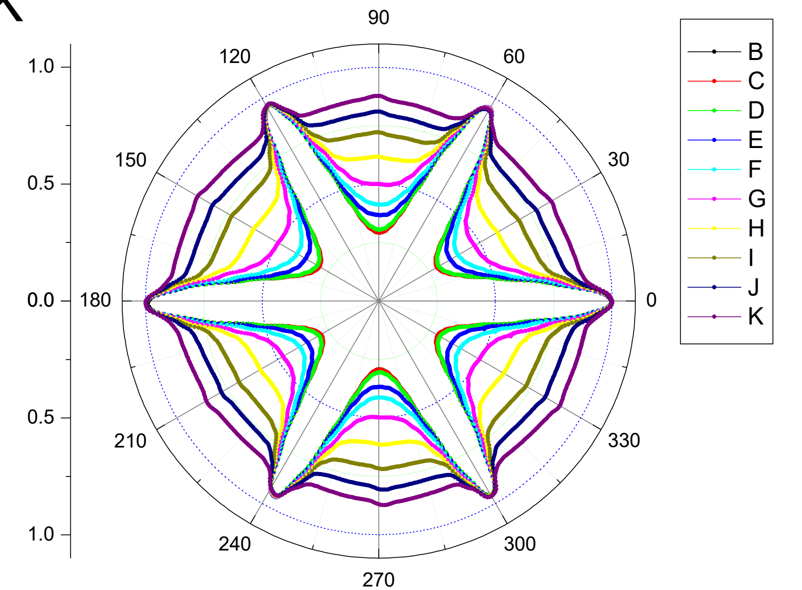
- Extremely anisotropic and exceptionally large ($\mu_1 > 10^8$ $cm^2V^{-1}s^{-1}$)

Field dependence of normalized conductivity at fixed temperatures (1/2)

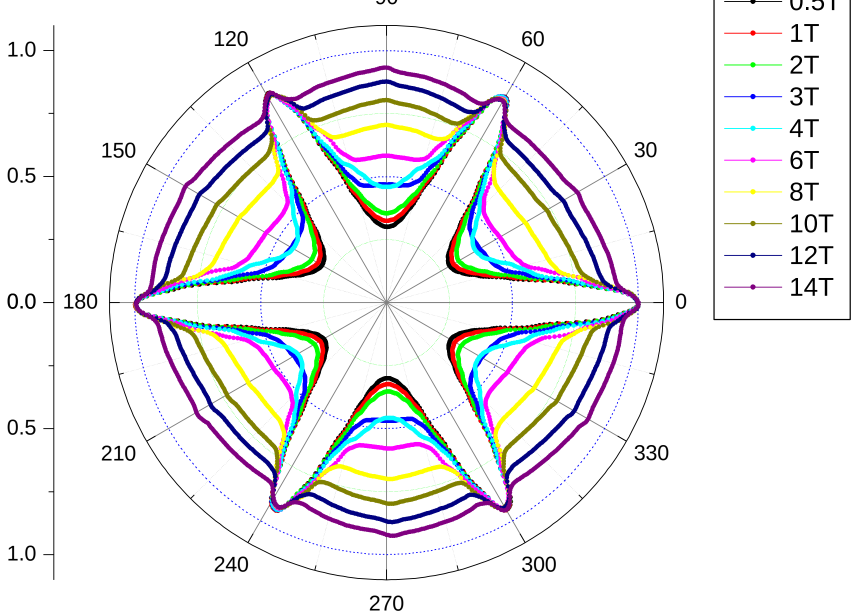
100K



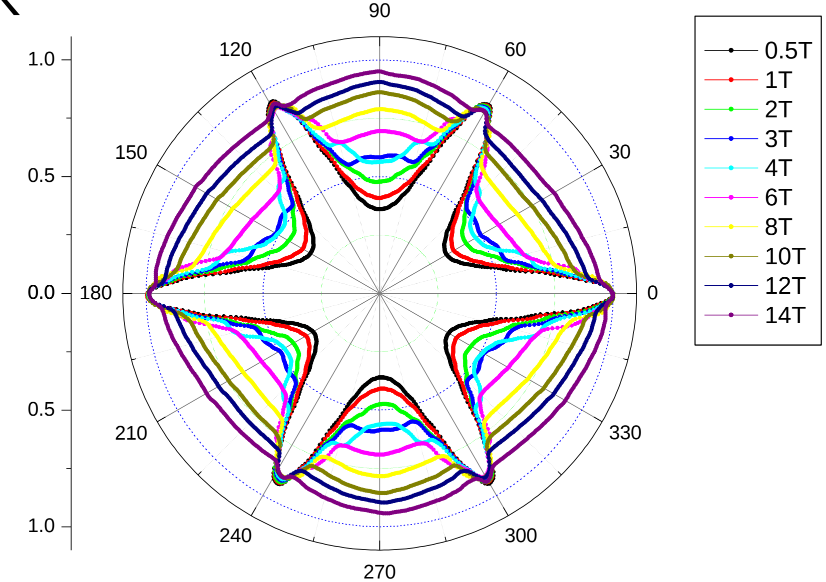
50K



30K

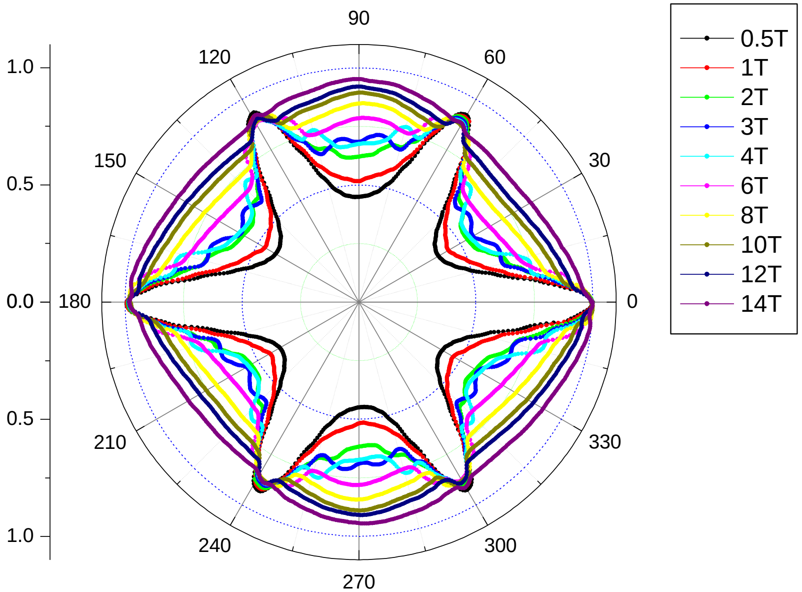


20K

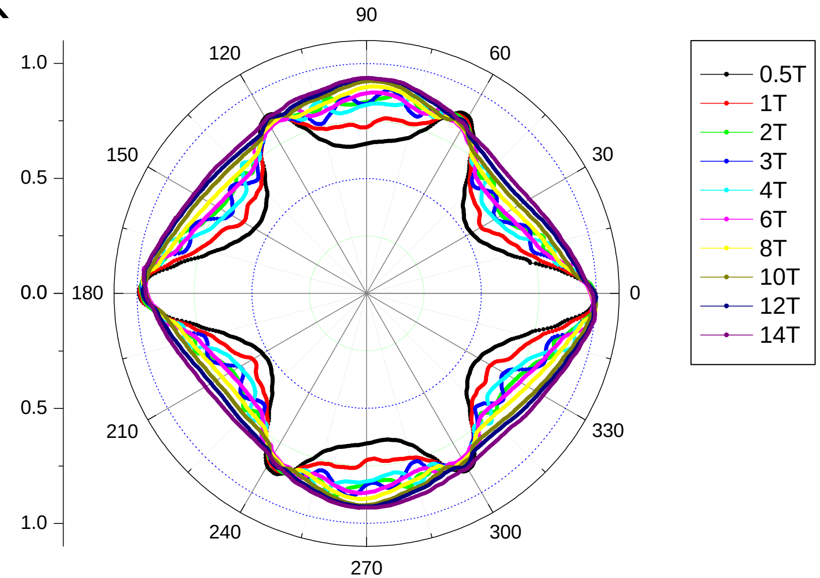


Field dependence of normalized conductivity at fixed temperatures (2/2)

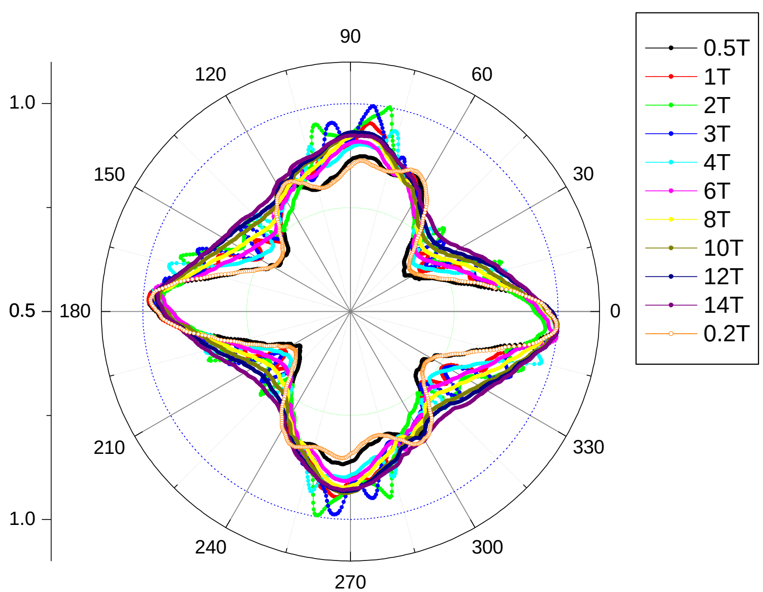
15K



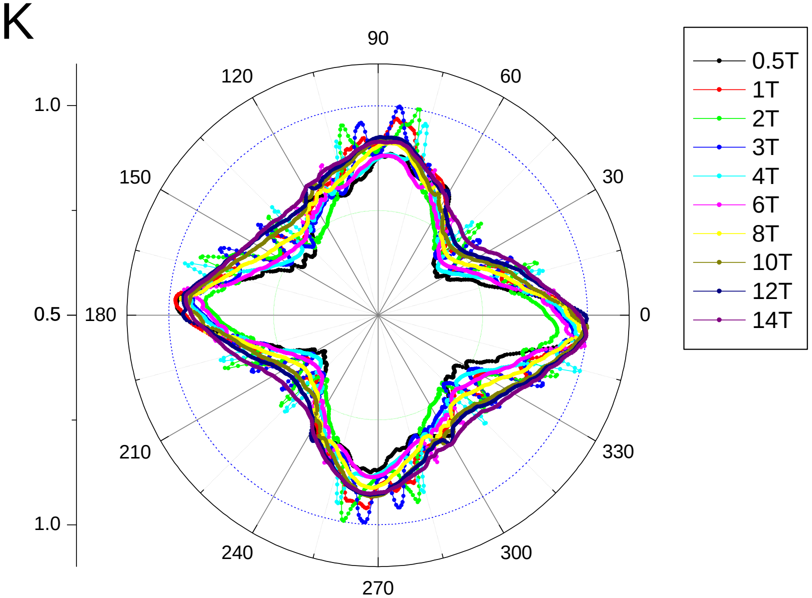
10K



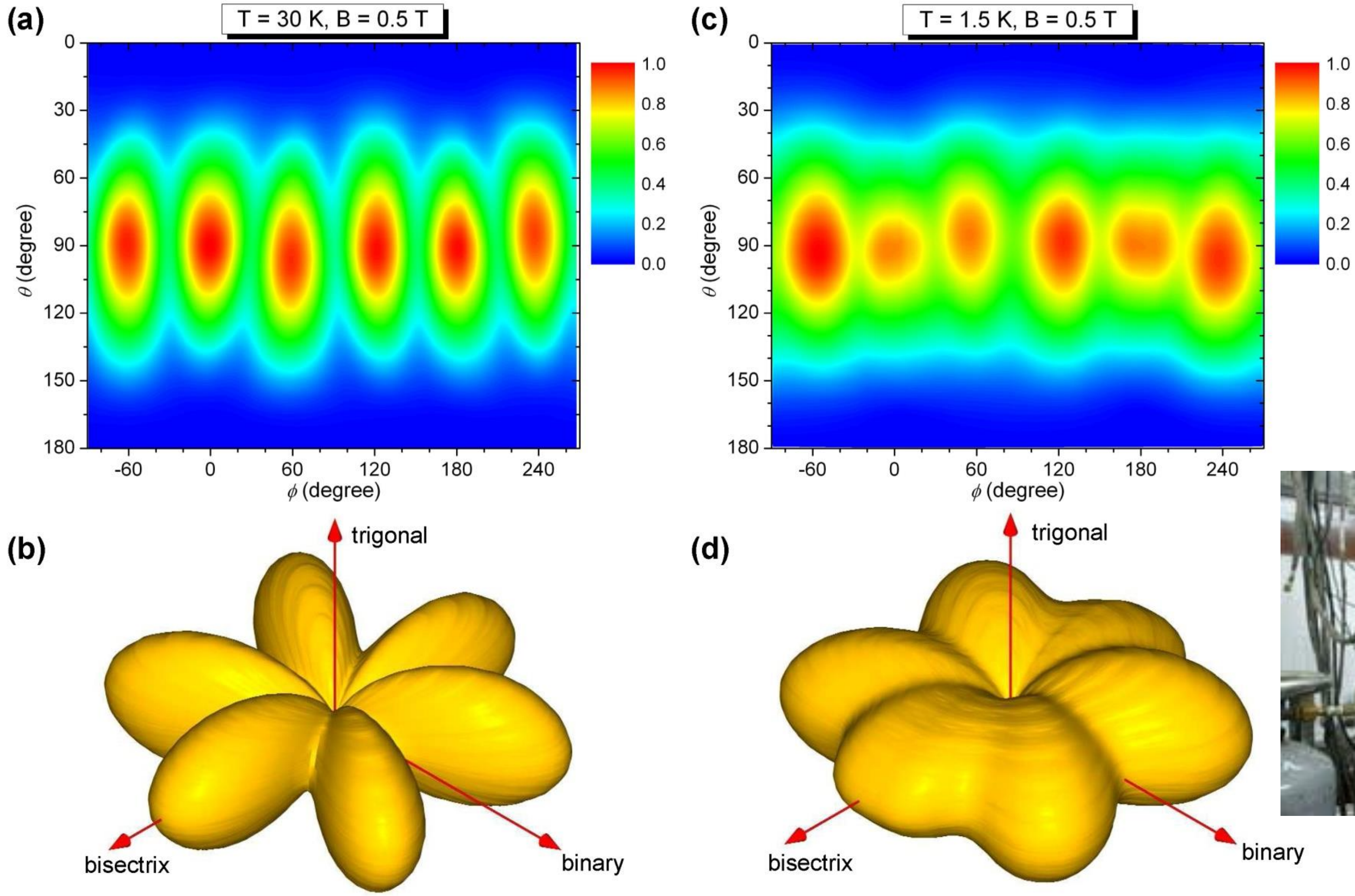
5K



1.4K



Two-axis rotation

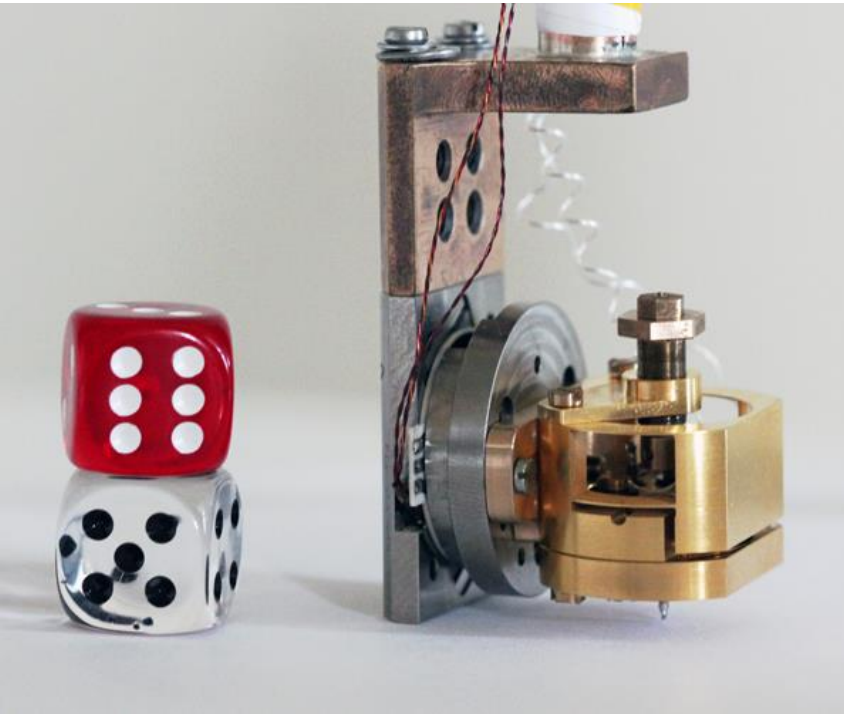


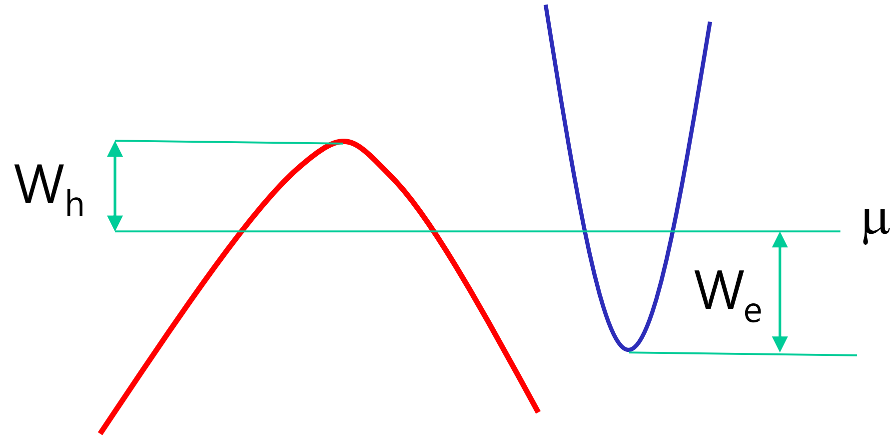
In all samples, the threefold symmetry of the crystal is spontaneously lost in low T and high B !

Possible origins:

- Internal strain ?
- Difference in mean-free-path along the three equivalent axes ?
- Coulomb interaction?

Magnetostriction in bismuth





$$\Delta F = F_{elastic} + \Delta N\,(W_e + W_h)$$

$W_e \propto \varepsilon$ $\quad$ $W_h \propto \varepsilon$

$F_{elastic} \propto \varepsilon^2$

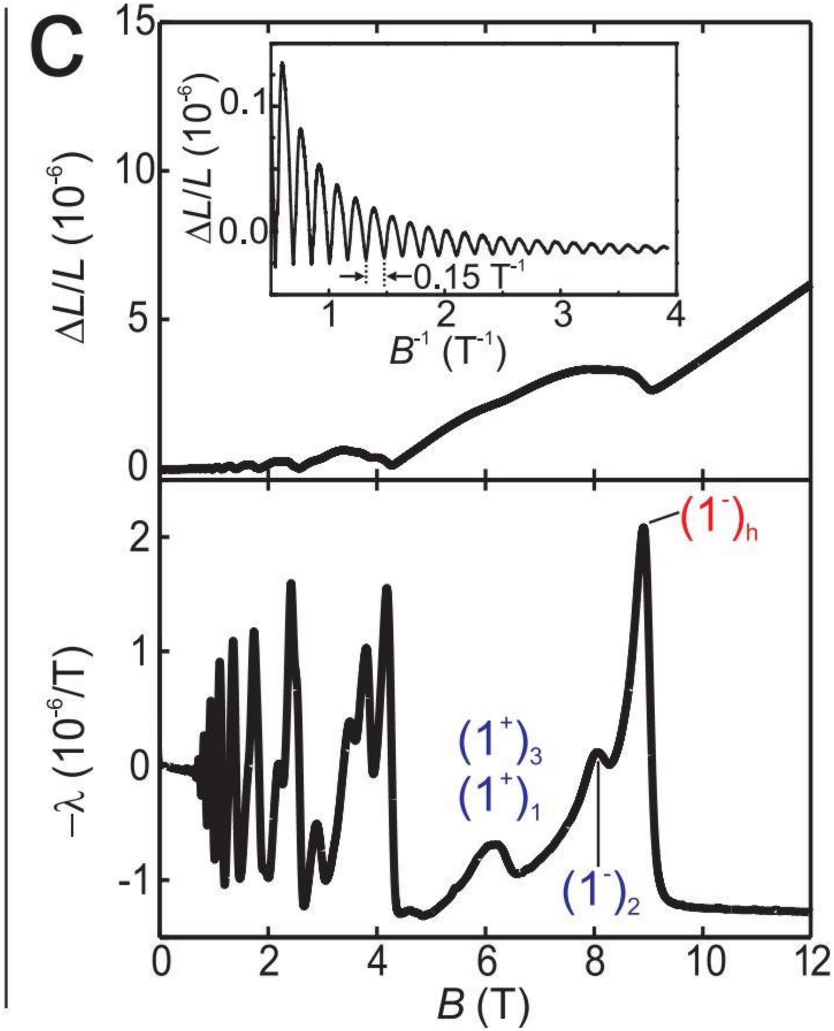
$\Delta F \propto a\,\varepsilon^2 - b\,\varepsilon$

Robert Küchler, Dresden
www.dialtometer.info

There is a finite $\varepsilon_{optimal}$ to minimize ΔF!

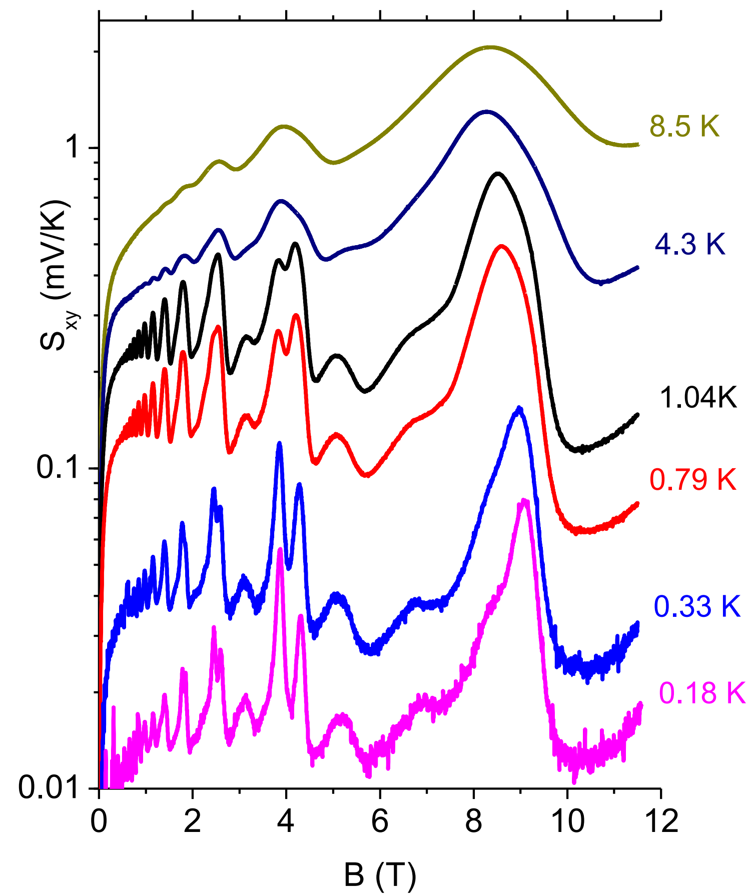
Quantum osillations for B//trigonal

Kuchler *et al.* , Nature Mat. 2014



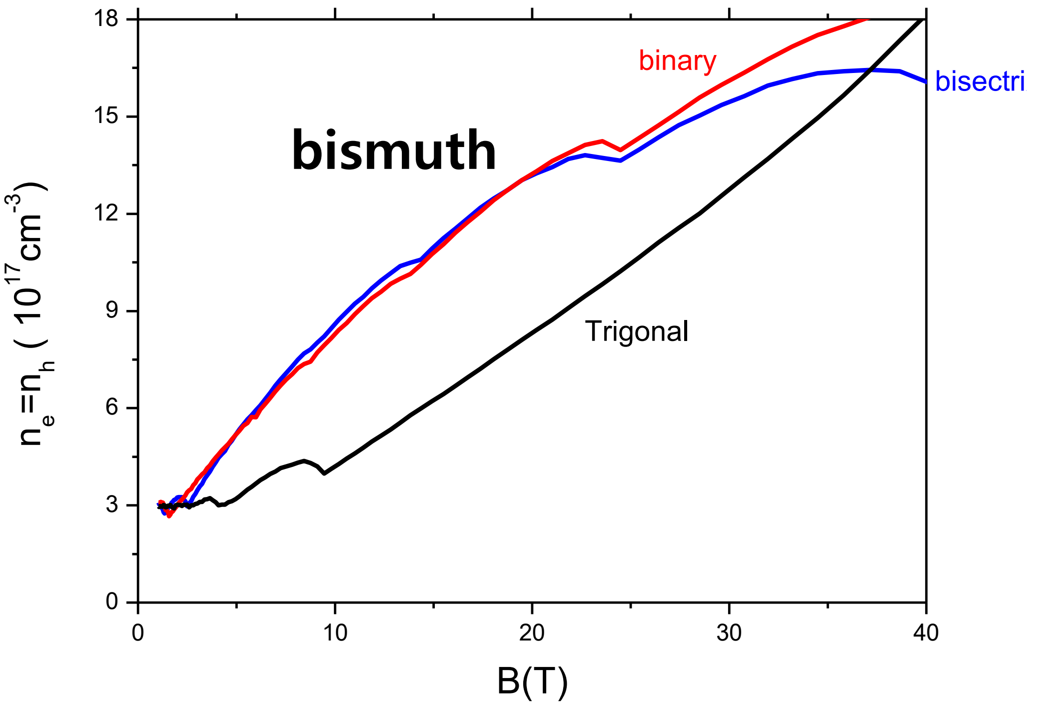
Magnetostriction

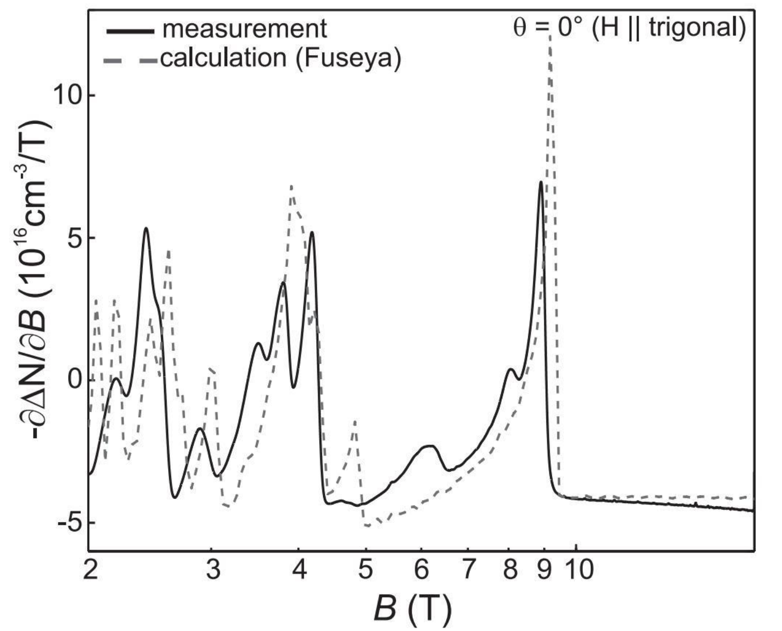
Zhu et al. PRB 2012



Nernst effect

Magnetostriction is caused by field-induced change in carrier concentration!





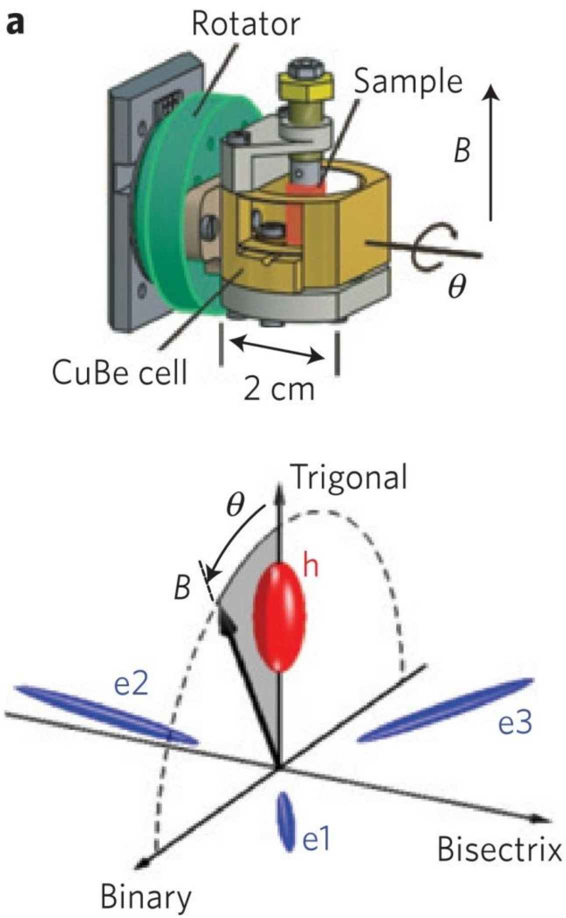
Degenerate Landau levels are voracious!

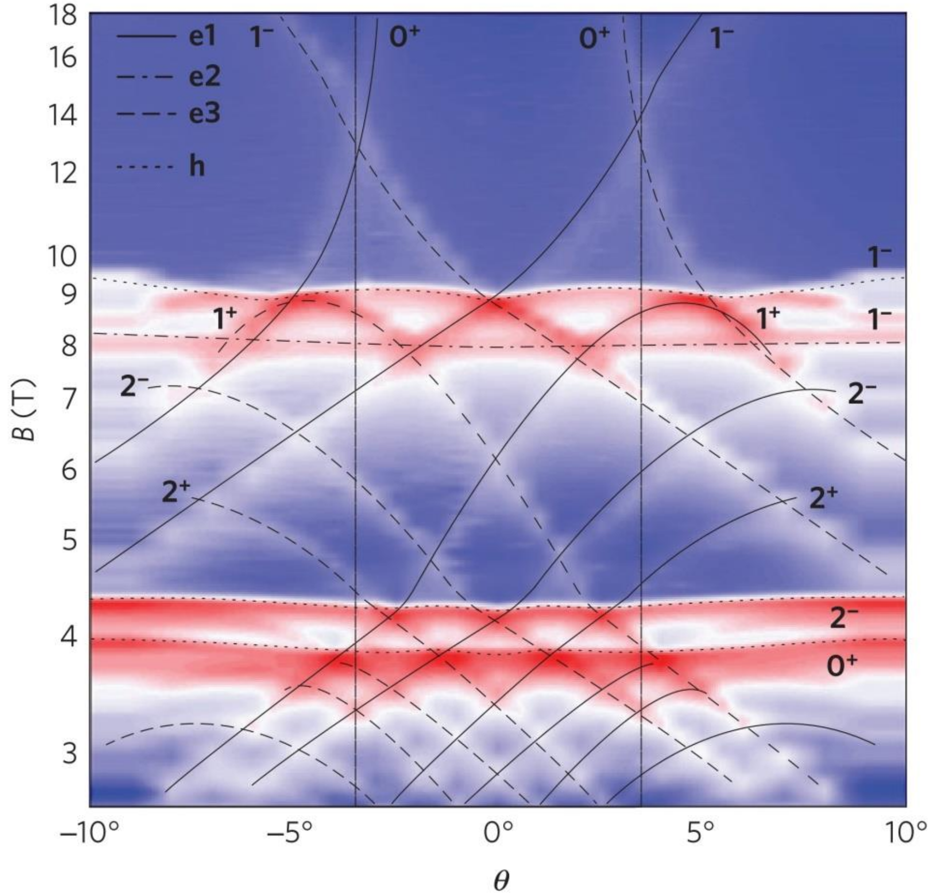
$$\varepsilon_{33} = c\,\Delta N$$

$$N(\varepsilon) = n/E_F \propto B$$

In a compensated system *n* can change without violating charge neutrality!

Angle-resolved Landau spectrum according to magnetostriction

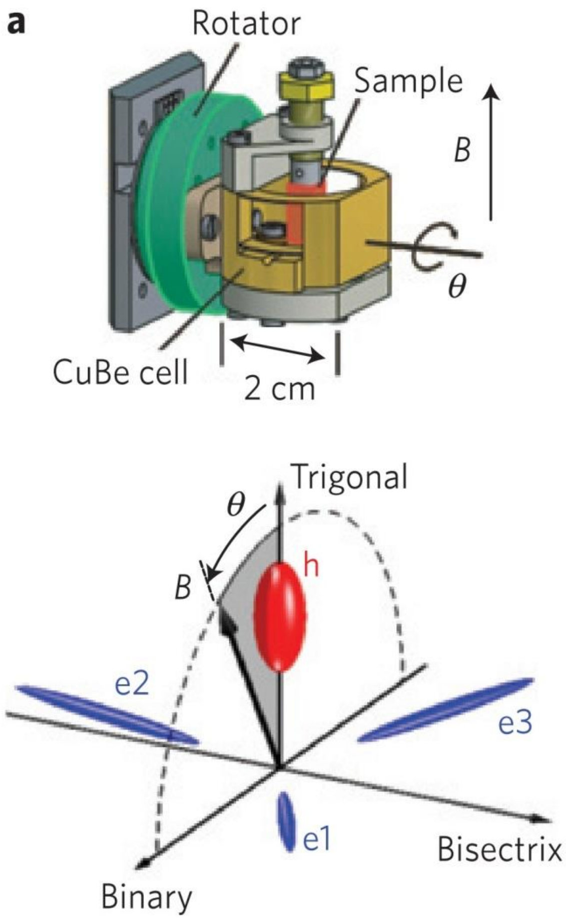




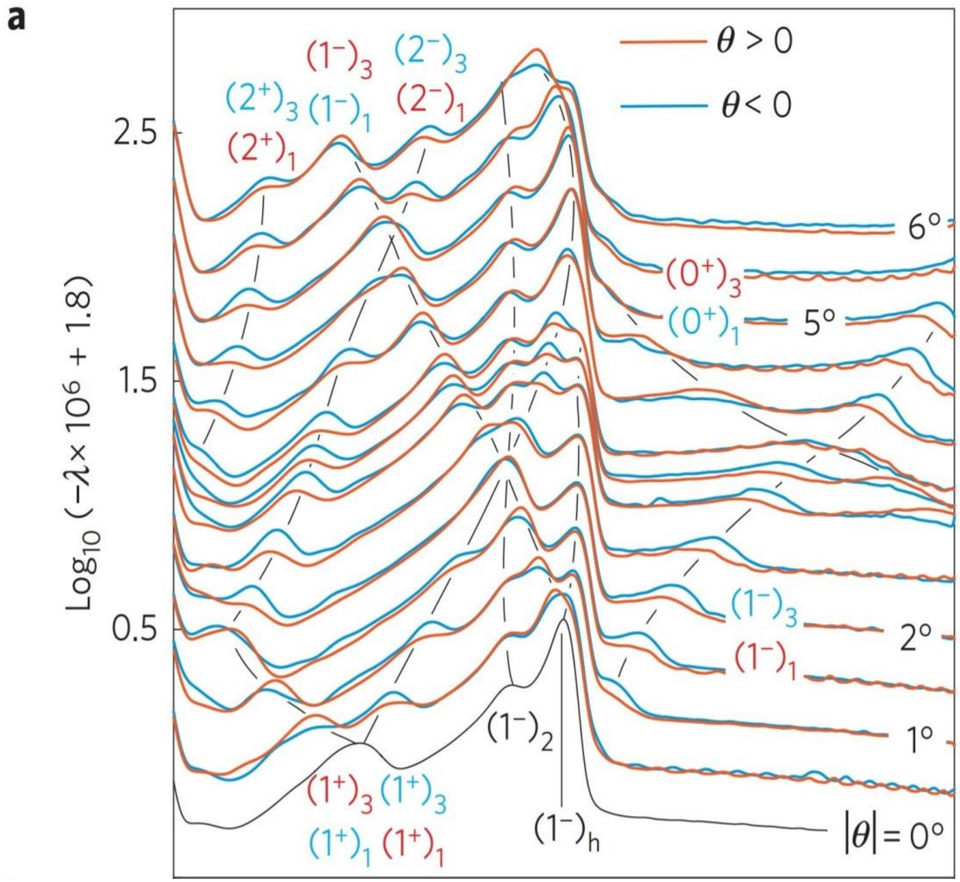
It is symmetric !

Kuchler *et al.* , Nature Mat. 2014

But density of states is valley-dependent



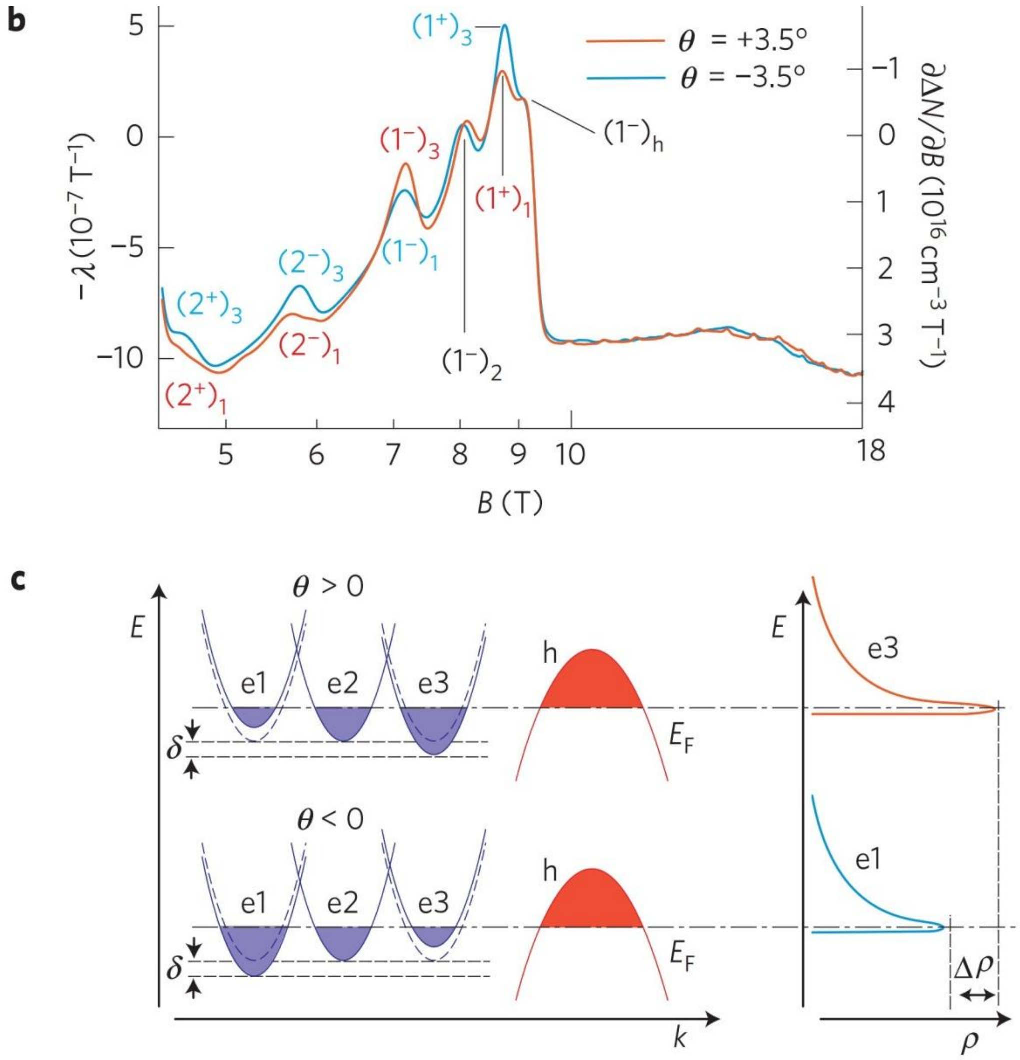
Kuchler *et al.* , Nature Mat. 2014



Compare peaks at negative and positive tilt angles!

Valley-dependent density of states

Different heights, but same positions!



Kuchler *et al.* , Nature Mat. 2014

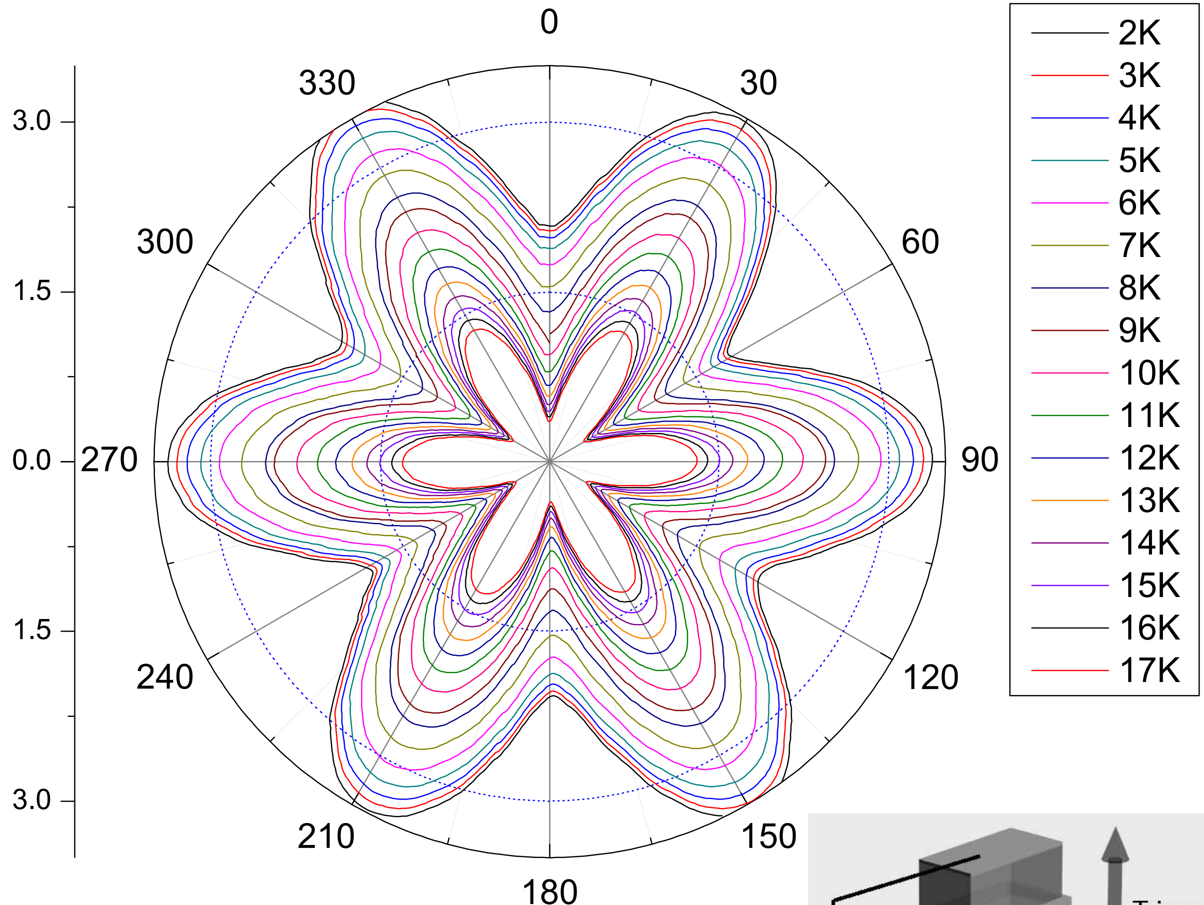
In all samples, the threefold symmetry of the crystal is spontaneously lost in low T and high B !

Possible origins:

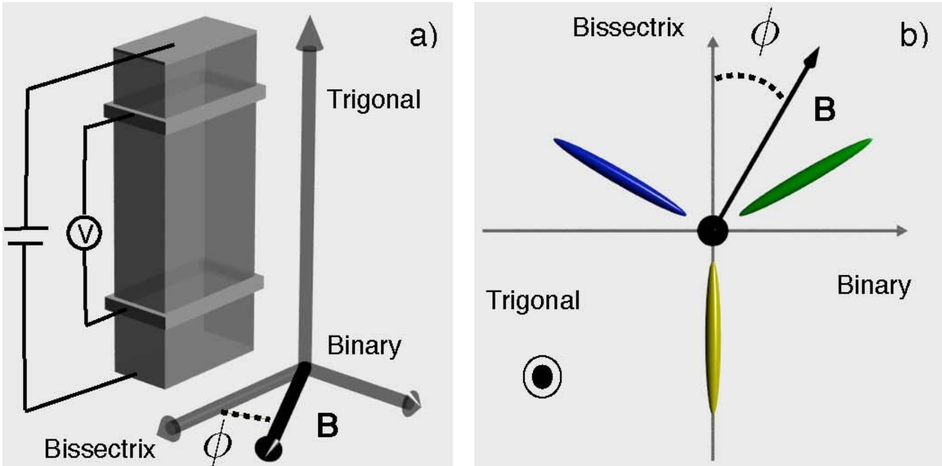
- ~~Internal strain ?~~
- ~~Difference in mean-free-path along the three equivalent axes ?~~
- Coulomb interaction?

But, is there a phase transition?

Back to resistivity!

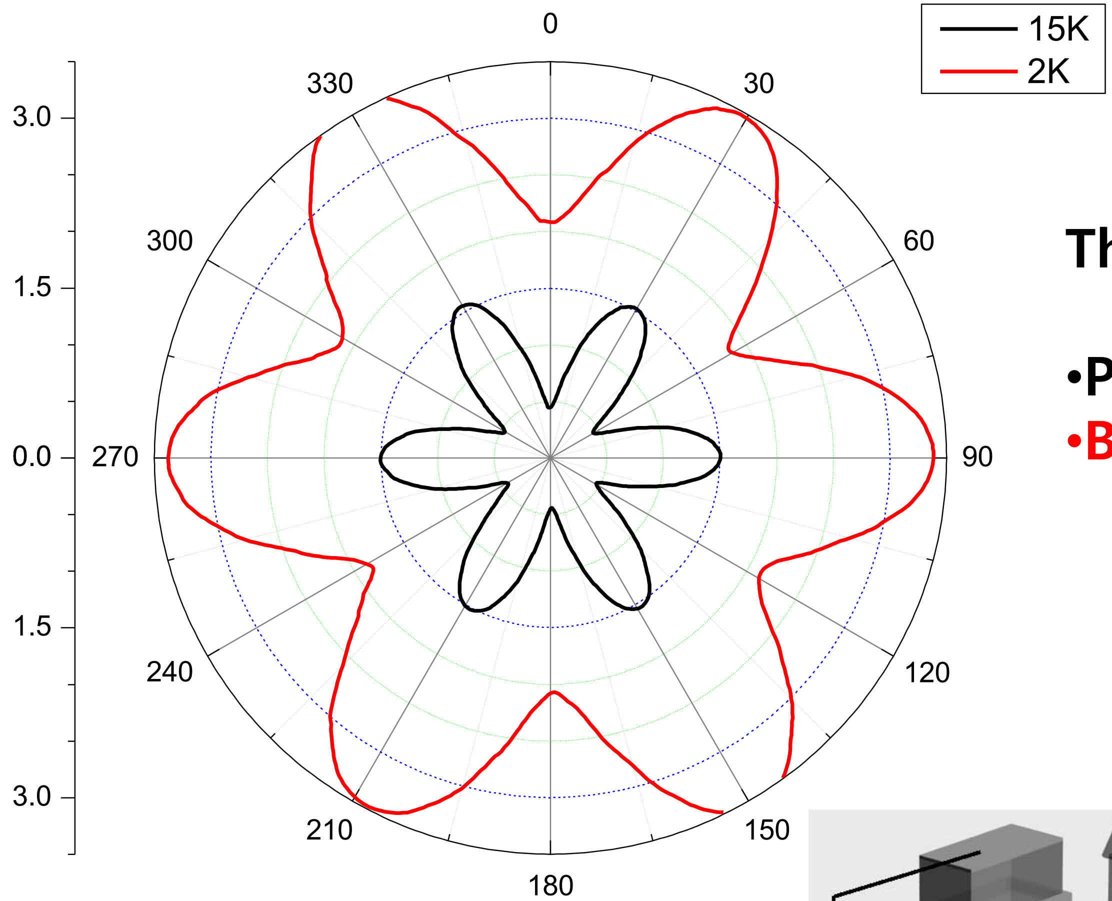


B=0.1 T



A. Collaudin *et al. PRX (2015)*

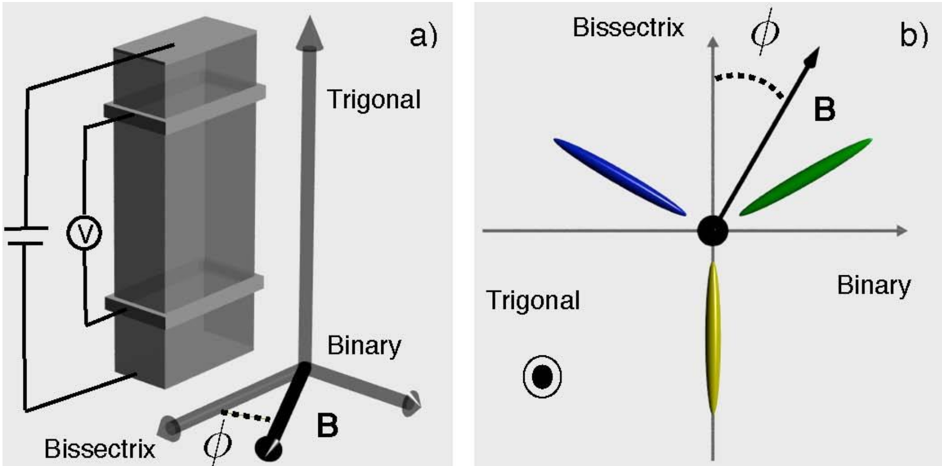
Back to resistivity!



Threefold symmetry is :

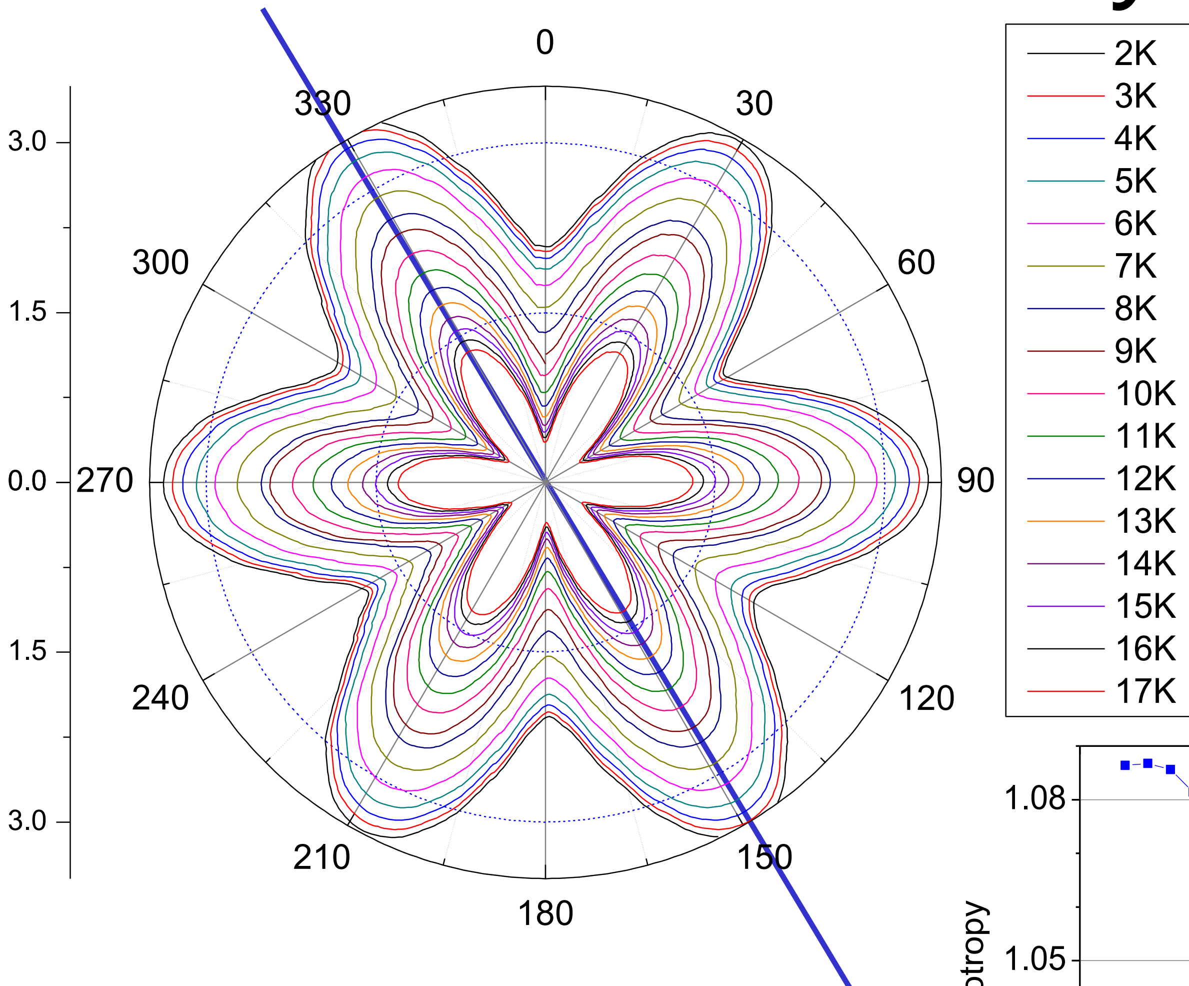
- **Present at 15 K**
- **But lost at 2 K**

B=0.1 T



A. Collaudin *et al. PRX(2015)*

Back to resistivity!



efold symmetry is :

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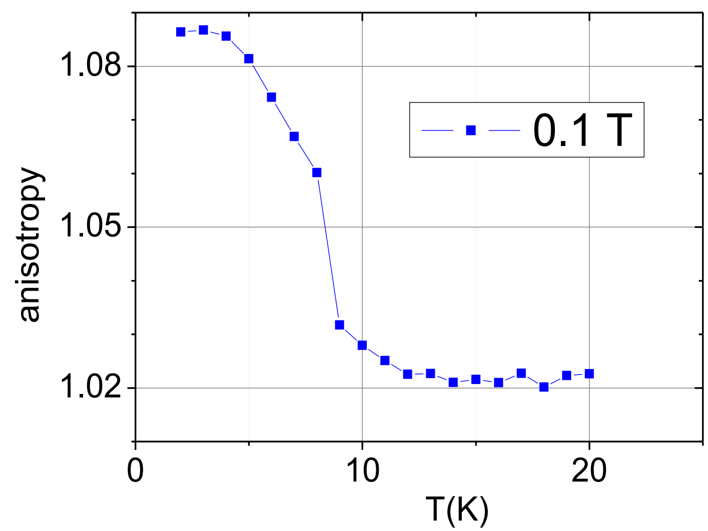
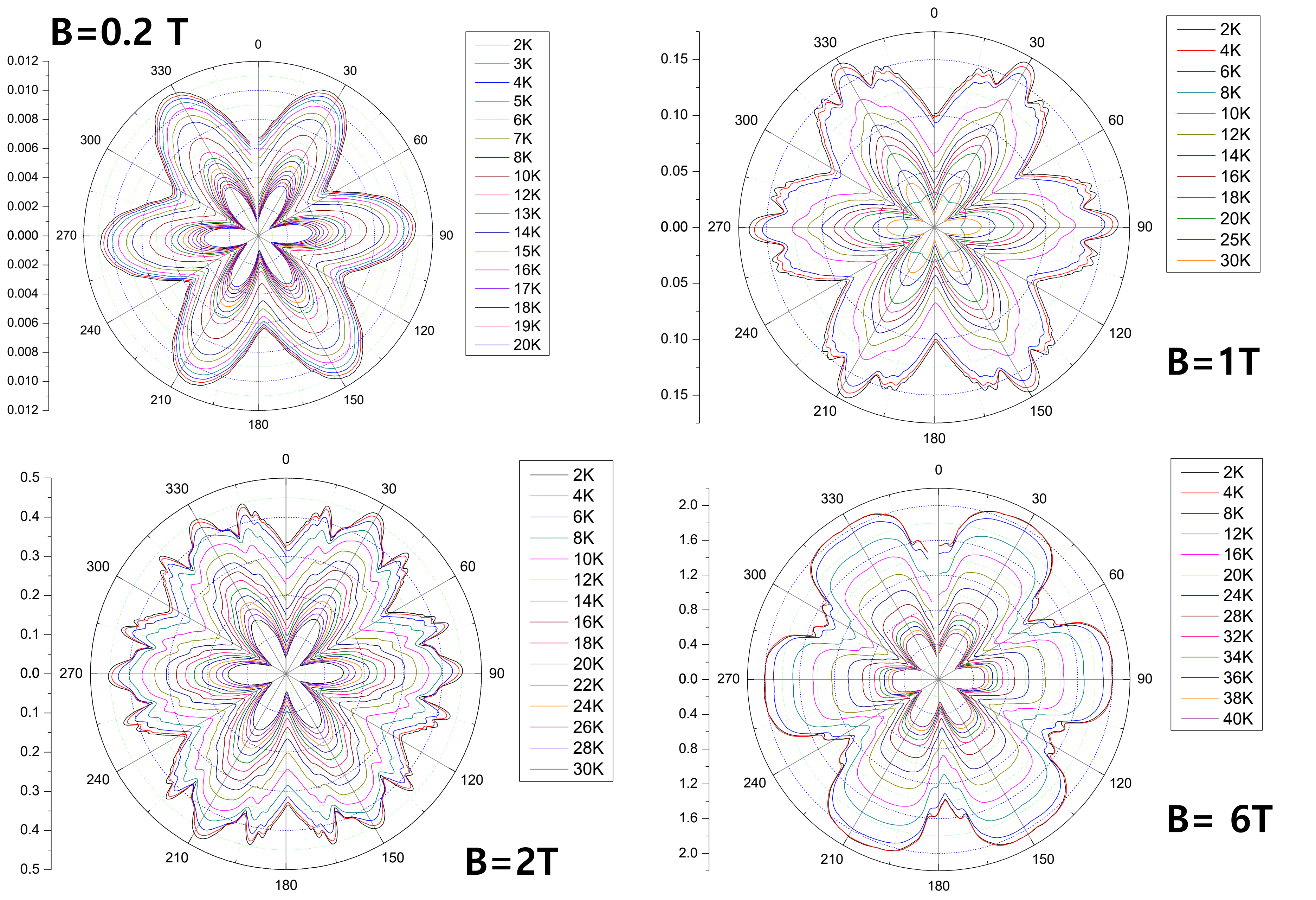
ost at 2 K

B=0.1 T



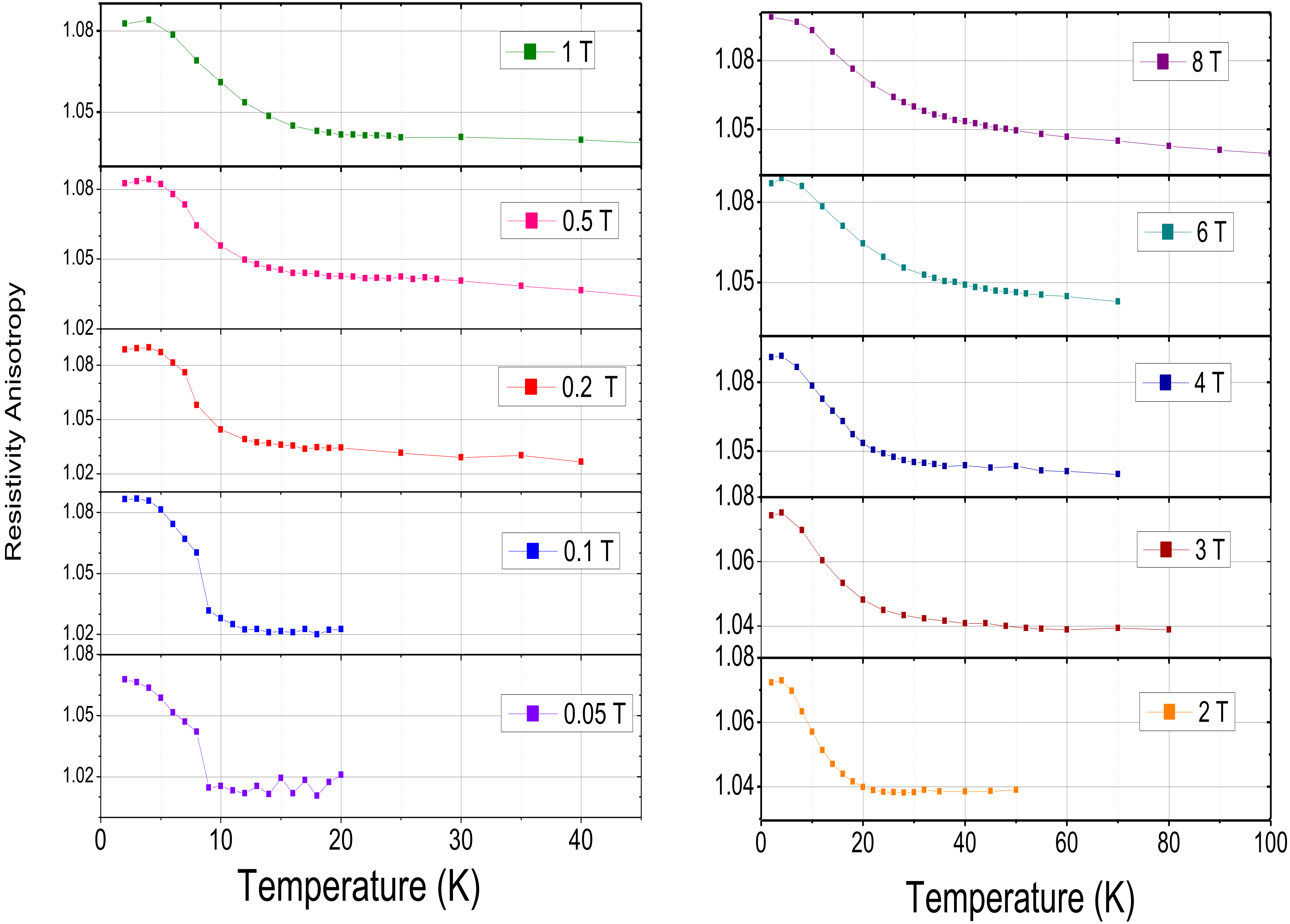
A. Collaudin *et al. PRX (2015)*

Evolution with magnetic field

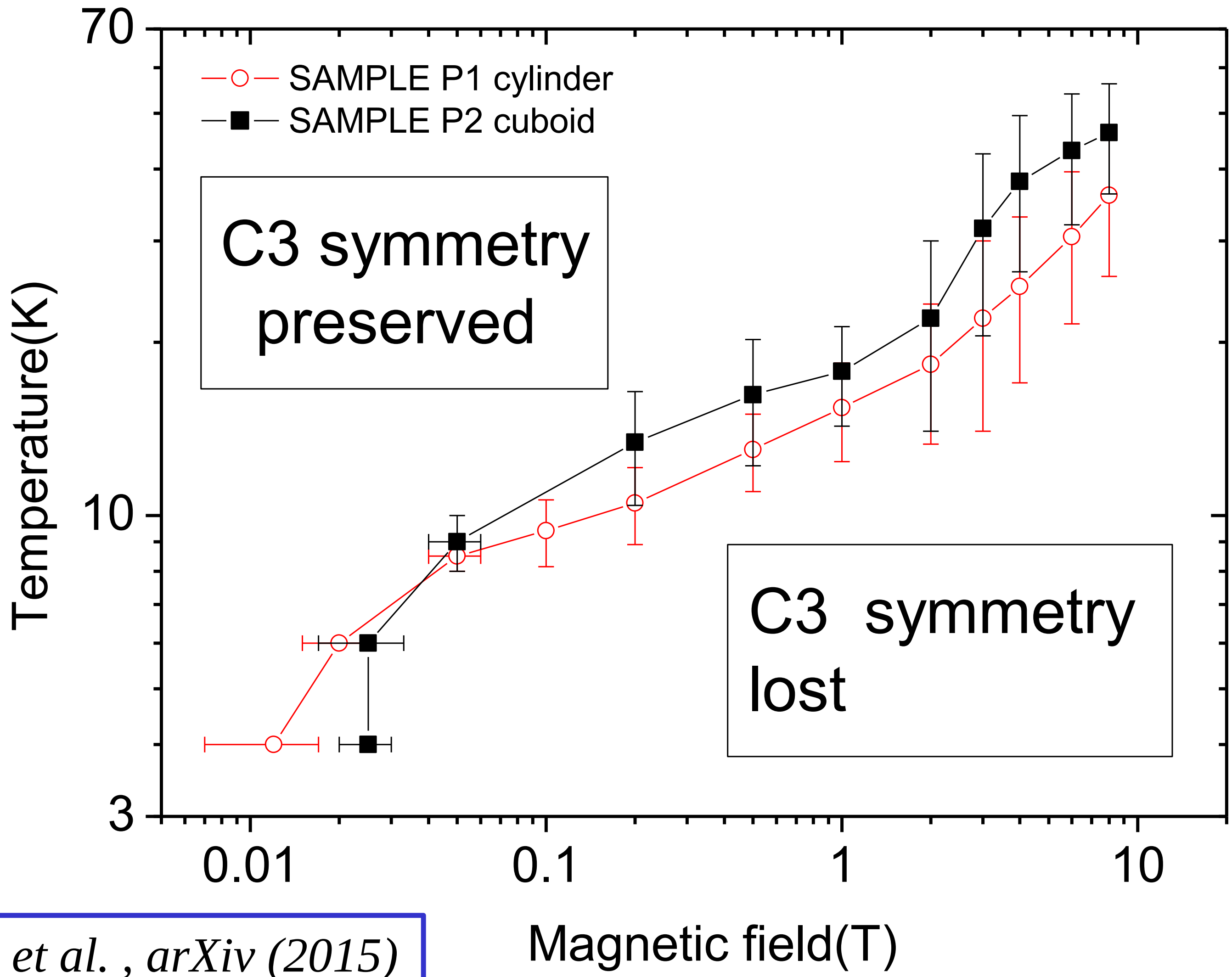


A. Collaudin *et al.* , *unpublished*

A phase transition



The phase diagram



A. Collaudin *et al.* , *arXiv (2015)*

PHYSICAL REVIEW B **82**, 035428 (2010)

Nematic valley ordering in quantum Hall systems

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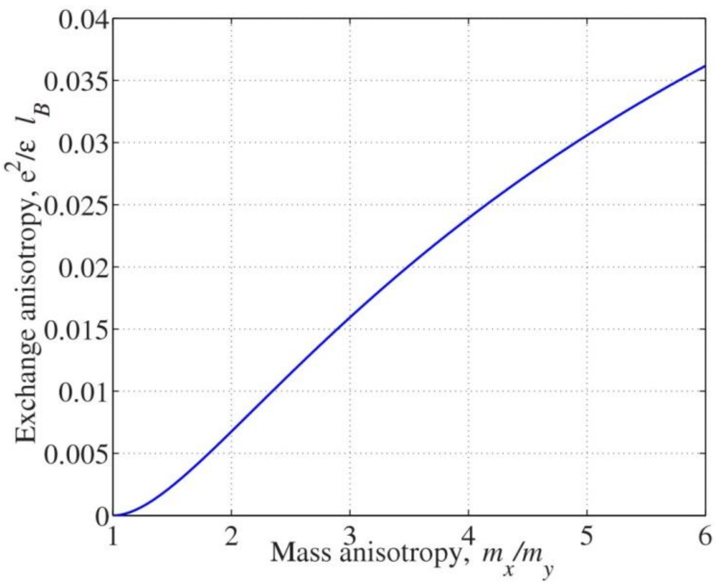
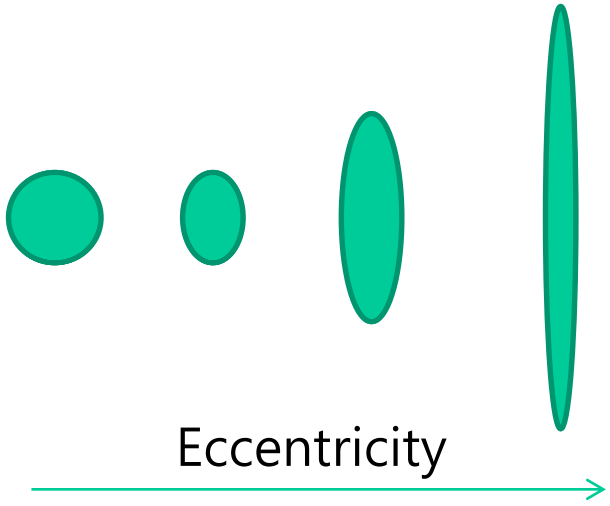
[1]*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*
[2]*Princeton Center for Theoretical Science, Princeton University, Princeton, New Jersey 08544, USA*
[3]*Department of Physics, Stanford University, Stanford, California 94305, USA*
(Received 23 March 2010; revised manuscript received 13 June 2010; published 20 July 2010)

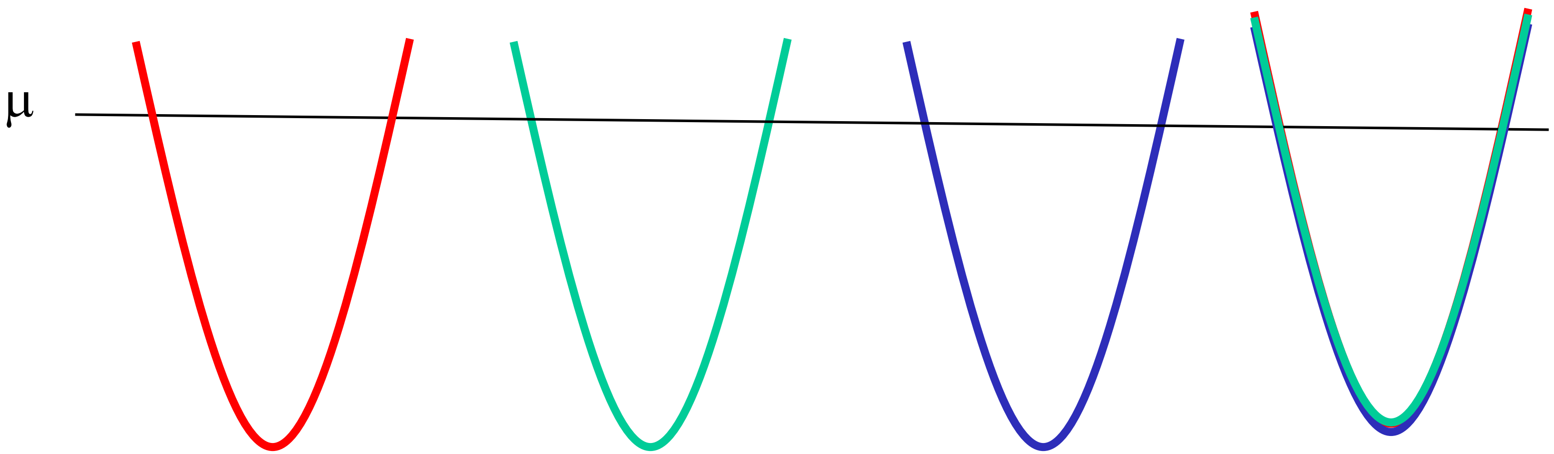
- Inequality in valley occupancy saves exchange energy!
- The effect is enhanced as the valleys become more eccentric!





Challenge to theory

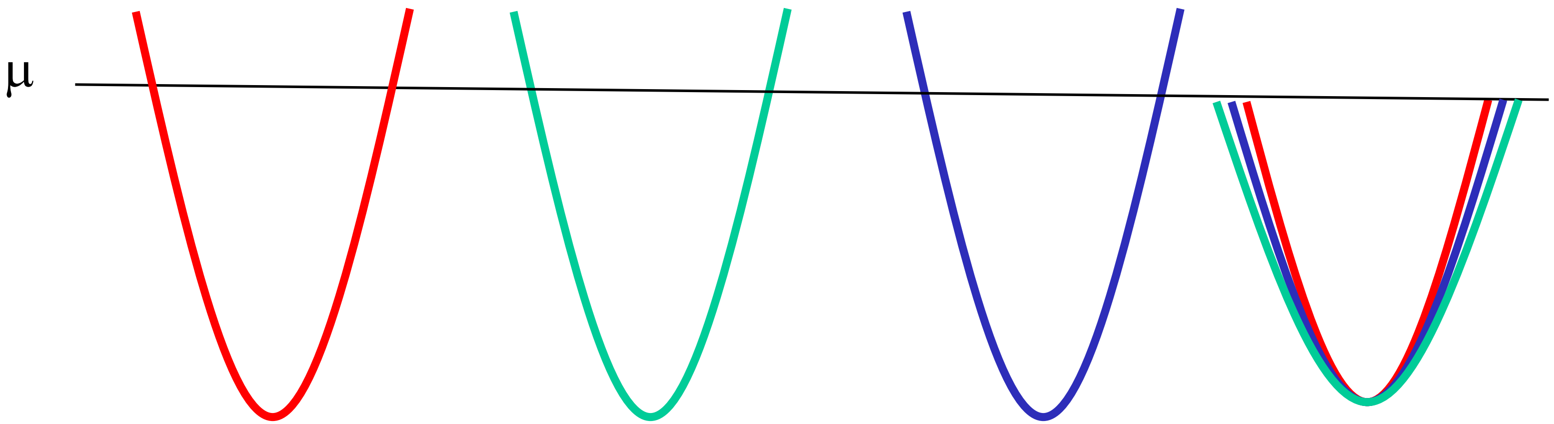
How does the magnetic field induce a gap between valleys' Landau levels near the Fermi energy?



Without interaction : The three valleys are degenerate

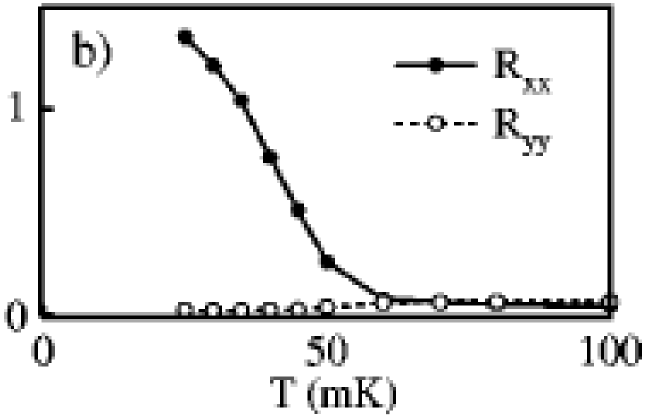
Challenge to theory

How does the magnetic field induce a gap between valleys' Landau levels near the Fermi energy?



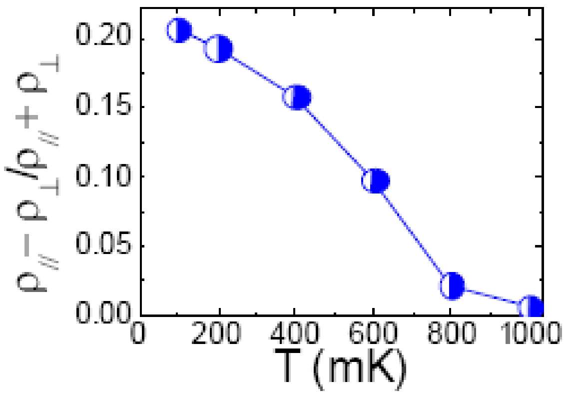
Interaction lifts degeneracy, but only near the chemical potential!

Nematic Fermi liquids



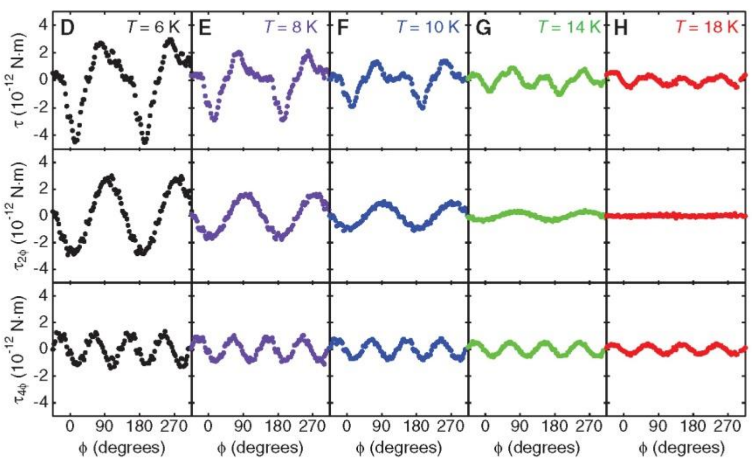
Lilly *et al.*, Phys. Rev. Lett. 82, 394 (1999)

Quantum Hall 2DEG



Borzi *et al.*, Science 315, 214 (2007)

Bulk layered $Sr_3Ru_2O_7$



Okazaki *et al.*, Science 331, 439 (2011)

Hidden order of URu_2Si_2

Nematic Fermi Fluids in Condensed Matter Physics

Annual Review of Condensed Matter Physics

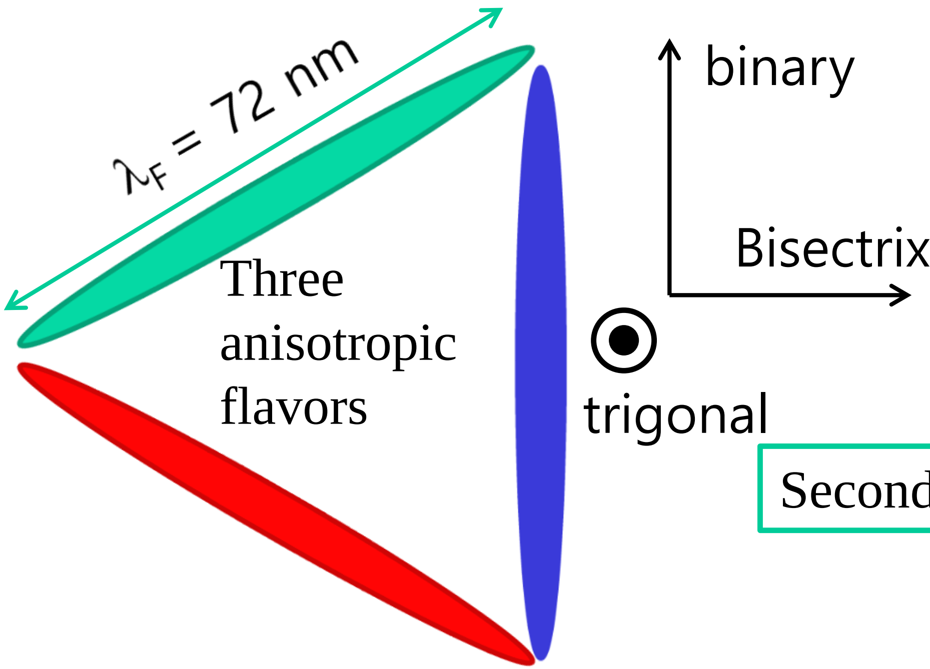
Eduardo Fradkin, Steven A. Kivelson, Michael J. Lawler
James P. Eisenstein, Andrew P. Mackenzie

"Classical nematics generally occur in liquids of rod-like molecules; given that electrons are point like, … motivation for contemplating electron nematics came from thinking of the electron fluid as a quantum melted electron crystal…"

View from real space

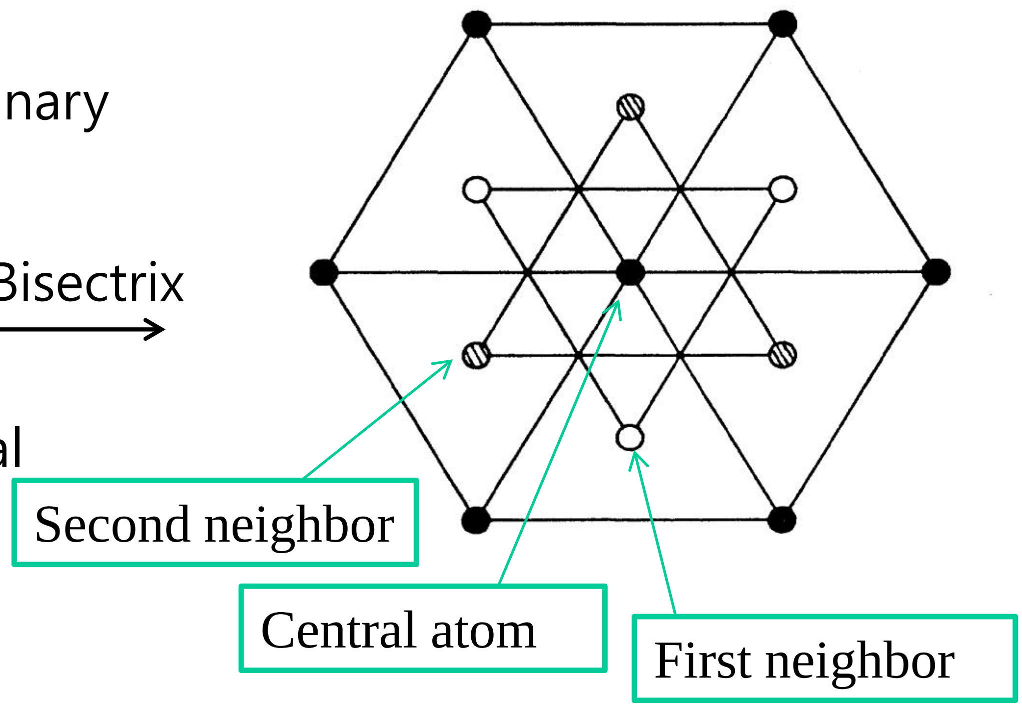
electrons

Interelectron distance~10-100 nm



atoms

Interatomic distance~0.3 nm



Rod-like electrons!

List of questions

- What makes such a low-symmety crystal structure stable?

The crystal floats over the liquid!

- Why magnetoresistance does not follow B-square?

- What causes the loss of rotational symmetry (or nematicity) induced by magnetic field?

- Can the melting temperature shift with magnetic field given the magnitude of Zeeman and cyclotron energies?