NANOSCALE NMR STUDIES OF TOPOLOGICAL INSULATORS,

<u>CRYSTALLINE INSULATORS AND DIRAC SEMIMETALS</u>

Louis Bouchard

UCLA

Mar. 22, 2019

TODAY’S TOPICS

Topological band structures

Topological Insulators

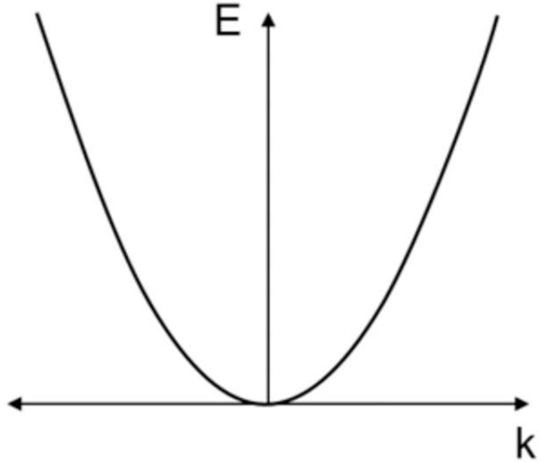
Topological Crystalline Insulators

Dirac Semimetals

Electrons In Crystals

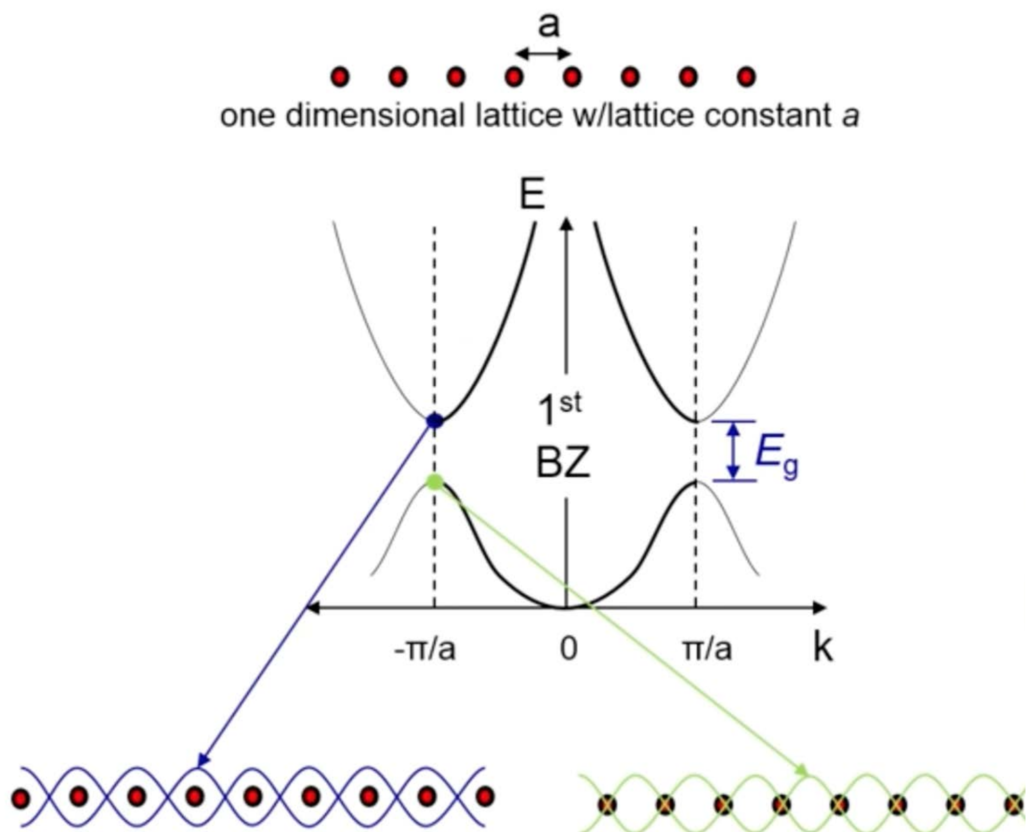
Electrons are waves

Free electrons



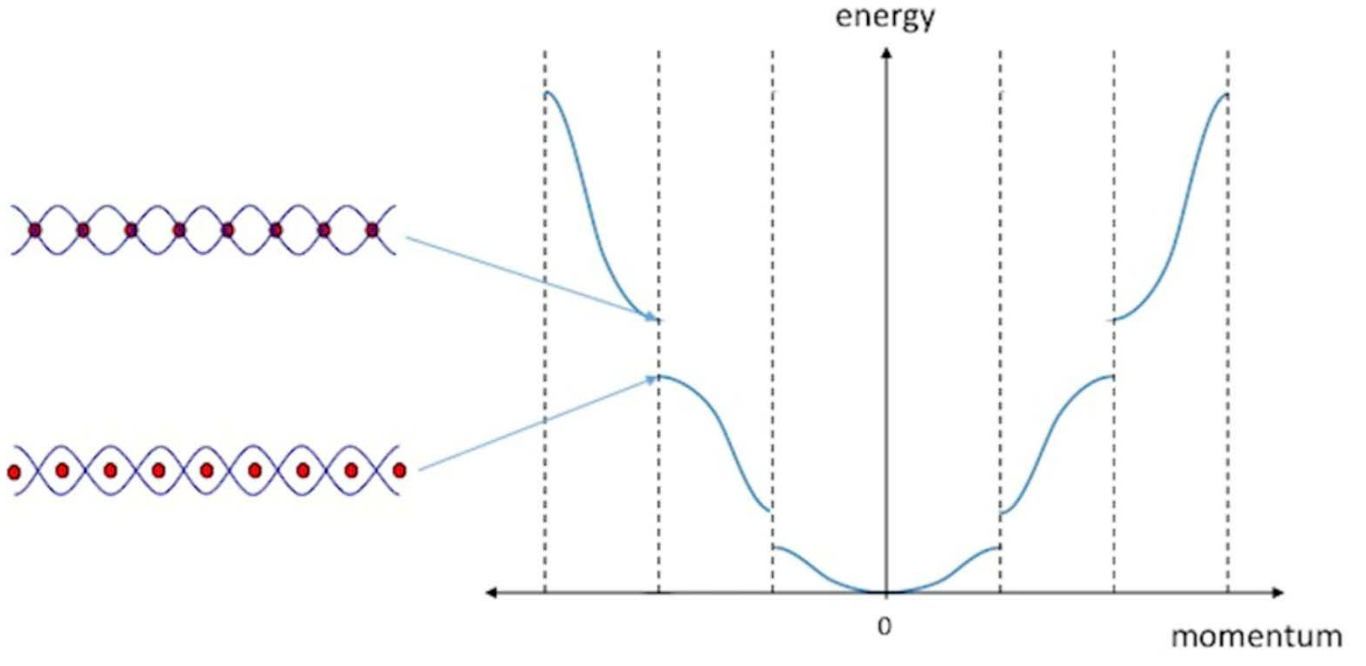
$$H = \frac{\hbar^2 k^2}{2m}$$

Nearly free electrons



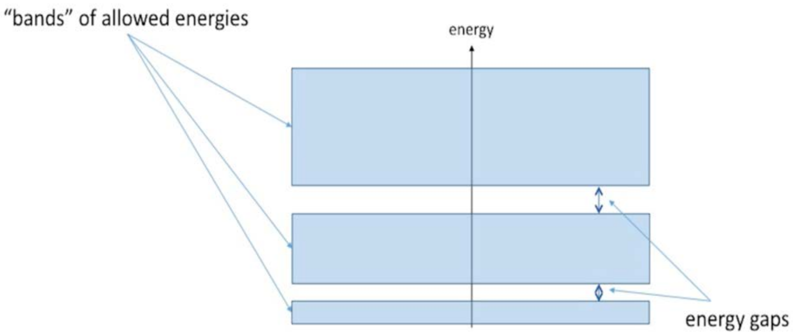
Things happen when e^- k = lattice spacing

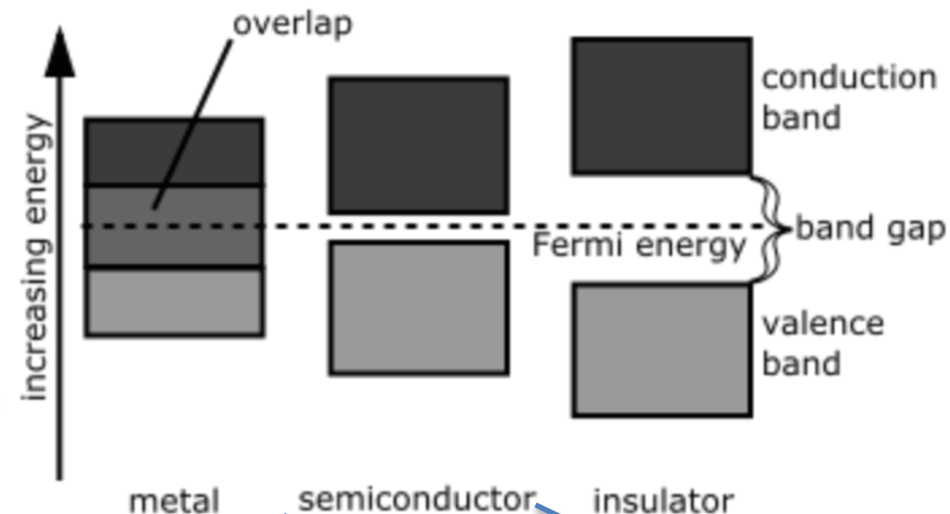
Electrons In Crystals: Things Happen When e$^-$ k = Lattice Spacing

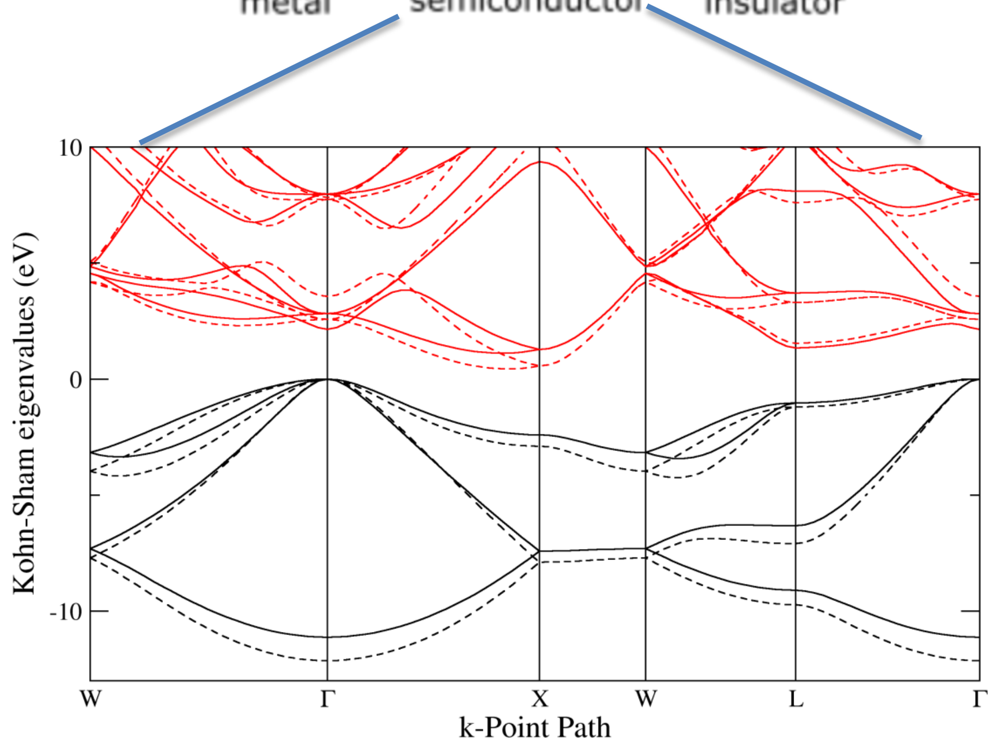


e$^-$ like to be on top of atoms (lowers energy),
but not in between (higher energy)

Band Theory of Solids

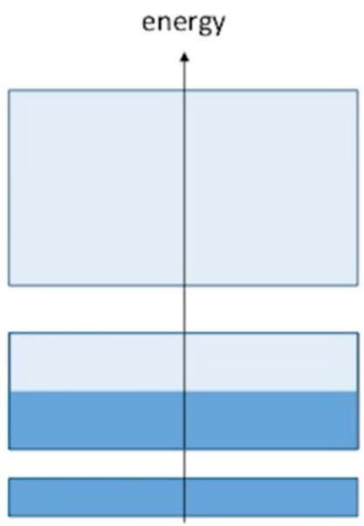




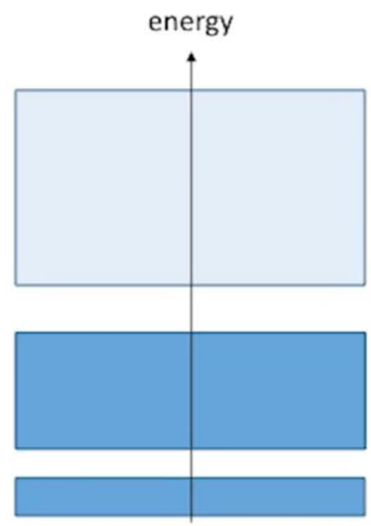


Si

Macroscopic Solid: Add e^- Fills Bands



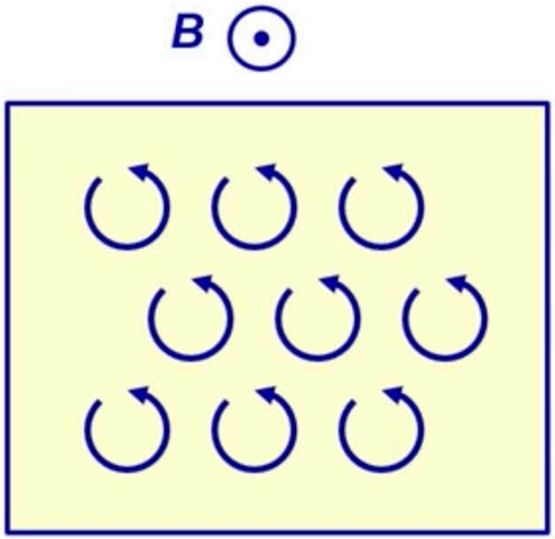
metal:
conducts electricity



insulator:
doesn’t conduct electricity

Insulators: e^- move around but no net movement

2D Metal in Magnetic Field



$$\left[\frac{(\mathbf{p}+e\mathbf{A})^2}{2m}\right]\Psi = E\Psi$$

$$\mathbf{A} = By\hat{\mathbf{x}}$$

$$\left[\frac{(p_x+eBy)^2}{2m}+\frac{p_y^2}{2m}\right]\Psi = E\Psi$$

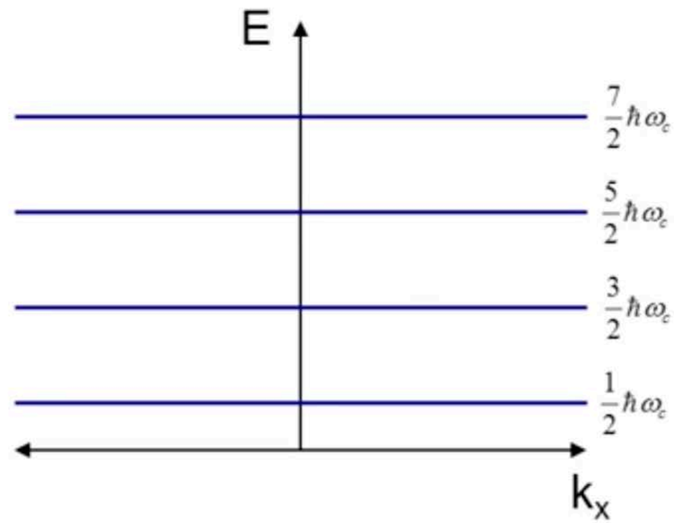
$$\Psi = e^{ik_x x}\chi(y)$$

$$\left[\frac{p_y^2}{2m}-\frac{1}{2}m\omega_c^2(y+y_k)^2\right]\chi(y) = E\chi(y)$$

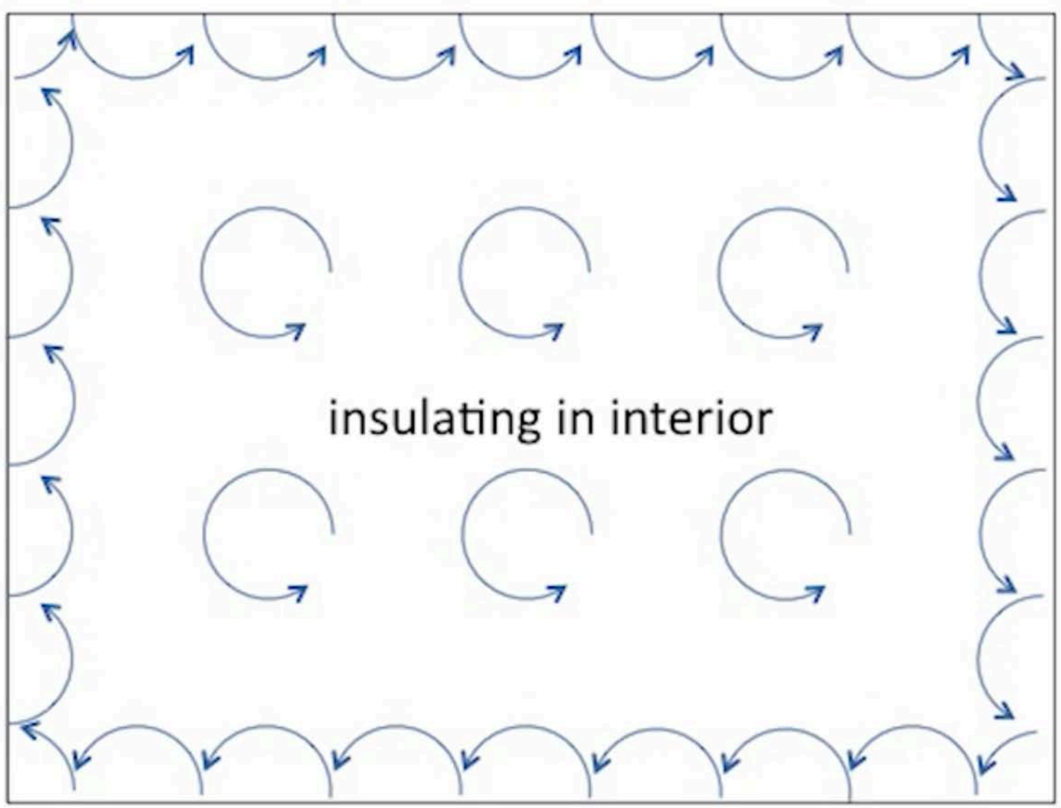
Solutions are harmonic oscillators
Localized in space, $v_{group} = 0$
Highly degenerate with discrete energies:

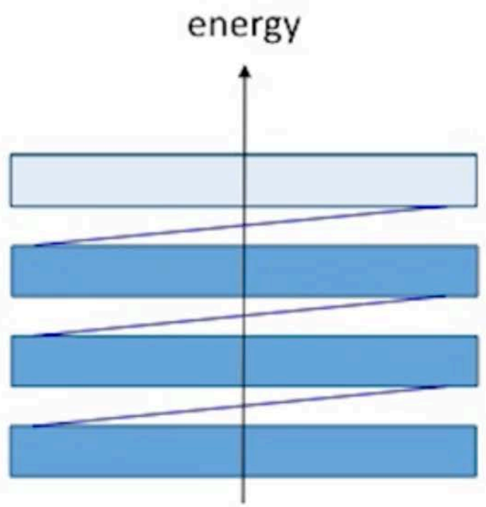
$$E = \left(n+\frac{1}{2}\right)\hbar\omega_c \qquad \omega_c = \frac{eB}{m}$$

"Landau levels"



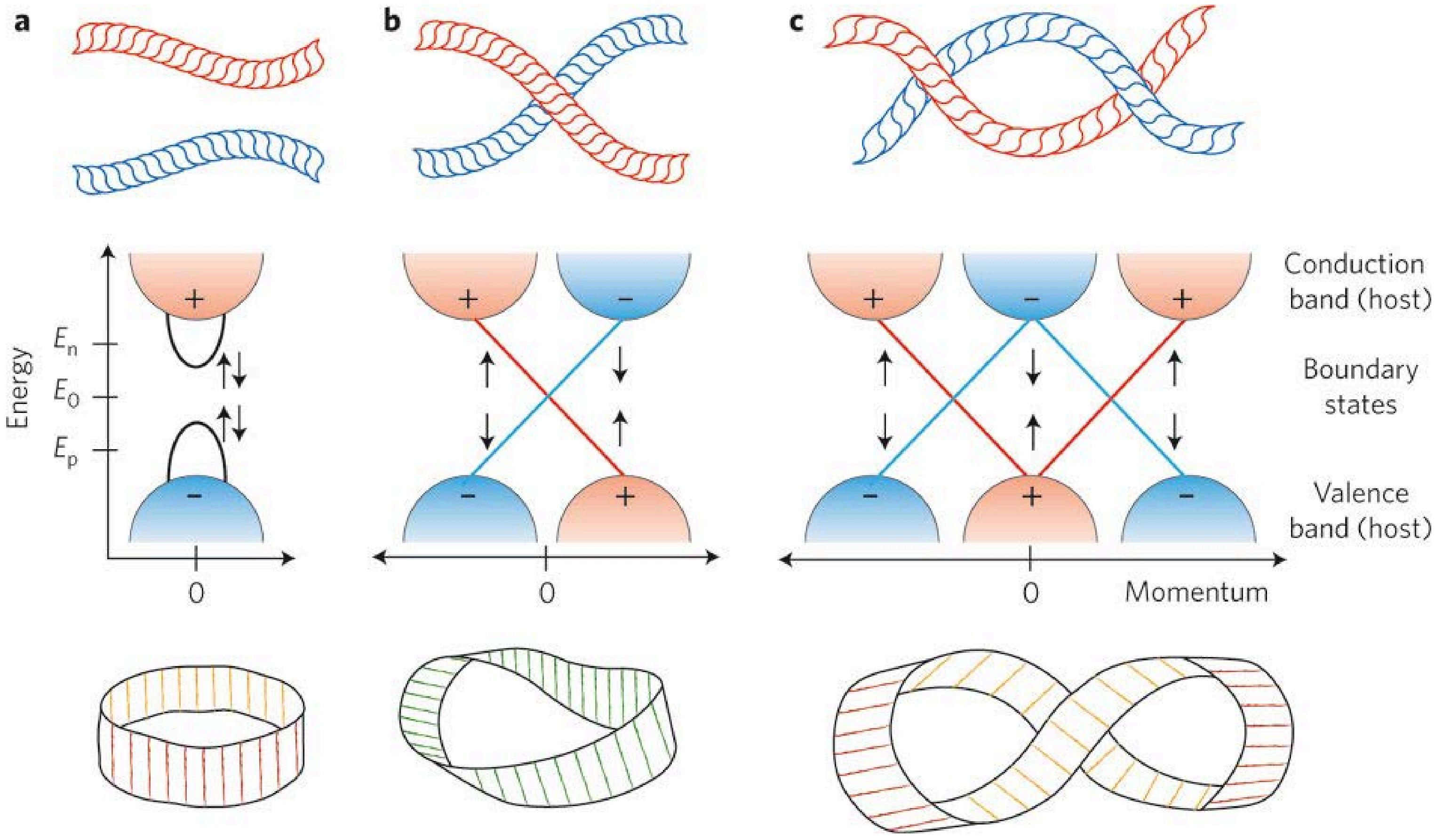
Topology: 1D Edge States Conduct Current





Boundaries are perfect conductors – no resistance

TI & Topological Invariant



H.C. Manoharan, Nature Nanotechnology 5, 477–479 (2010)

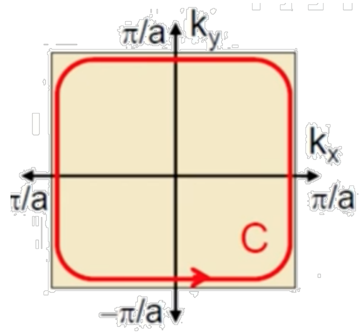
TKNN: Topological Invariant for QHE

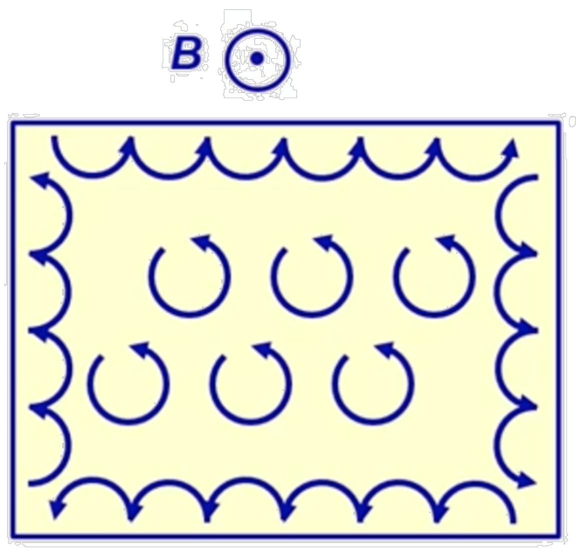
Berry connection $\mathbf{A}(\mathbf{k}) = -i\langle u_i(\mathbf{k})|\nabla_k|u_i(\mathbf{k})\rangle$

Berry curvature $\mathbf{F}(\mathbf{k}) = \nabla_k \times \mathbf{A}(\mathbf{k})$

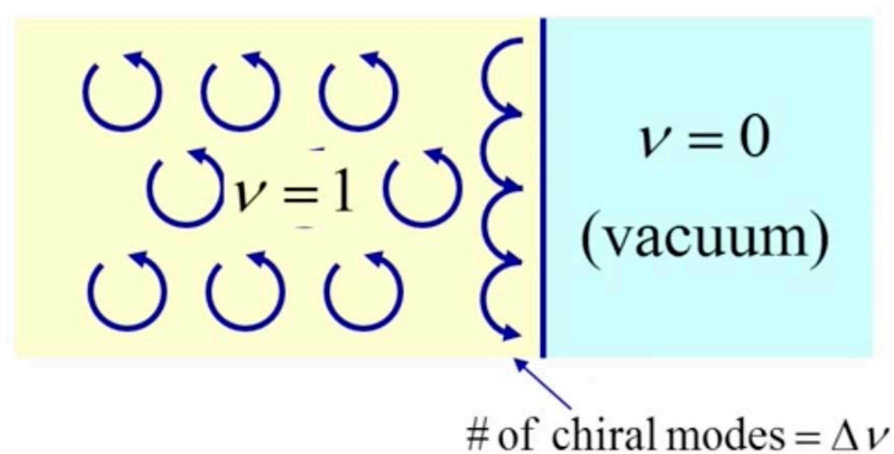
TKNN invariant $\nu = \frac{1}{2\pi}\oint_C \mathbf{A}(\mathbf{k})\cdot d\mathbf{k} = \frac{1}{2\pi}\int_{BZ} \mathbf{F}(\mathbf{k})\, d^2\mathbf{k}$

$$\boldsymbol{\sigma} = \begin{pmatrix} 0 & -\nu\frac{e^2}{h} \\ \nu\frac{e^2}{h} & 0 \end{pmatrix}$$

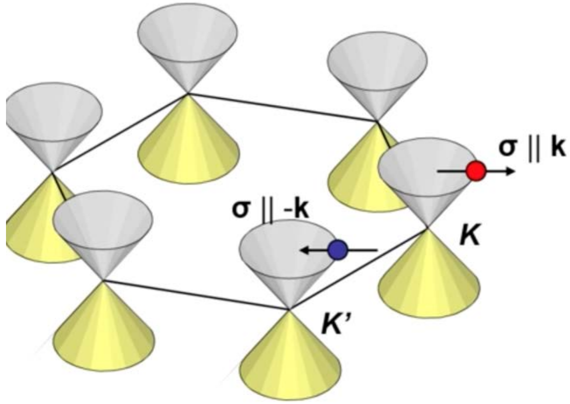




Edge-State Picture of QHE



Are Landau levels the only system with TKNN ν≠0?

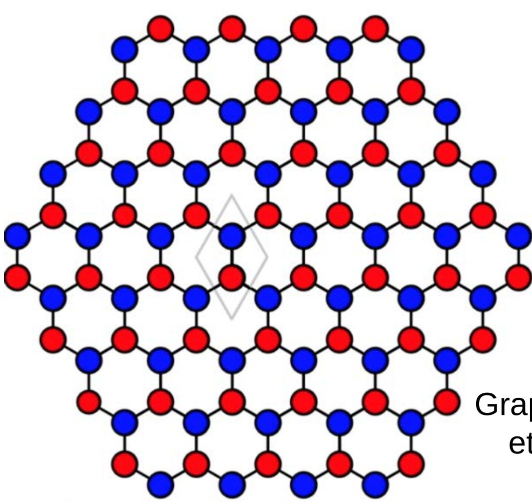


$$\hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \begin{pmatrix} F_A(r) \\ F_B(r) \end{pmatrix} = \varepsilon \begin{pmatrix} F_A(r) \\ F_B(r) \end{pmatrix}$$

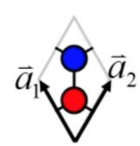
$$\hbar v_F (\boldsymbol{\sigma} \cdot \boldsymbol{k}) \boldsymbol{F}(r) = \varepsilon \boldsymbol{F}(r)$$

$$|k\rangle = \frac{1}{\sqrt{2}} \underbrace{\boxed{e^{i\mathbf{k}\cdot\mathbf{r}}}}_{\text{Plane wave}} \underbrace{\boxed{\begin{pmatrix} -ibe^{-i\theta_k/2} \\ e^{i\theta_k/2} \end{pmatrix}}}_{\text{spinor}}$$

Two *identical* atoms in unit cell: A B



unit cell:

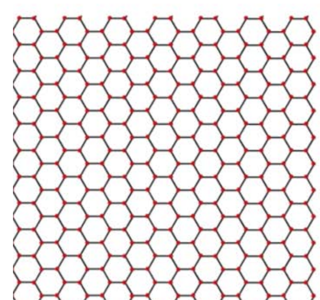


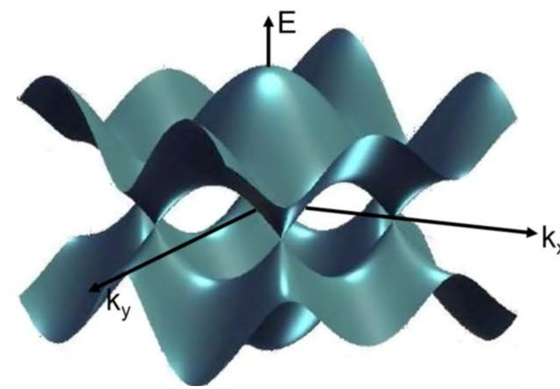
Two atoms

Graphene: Geim, Novoselov et al. PNAS 102, 10341 (2005)

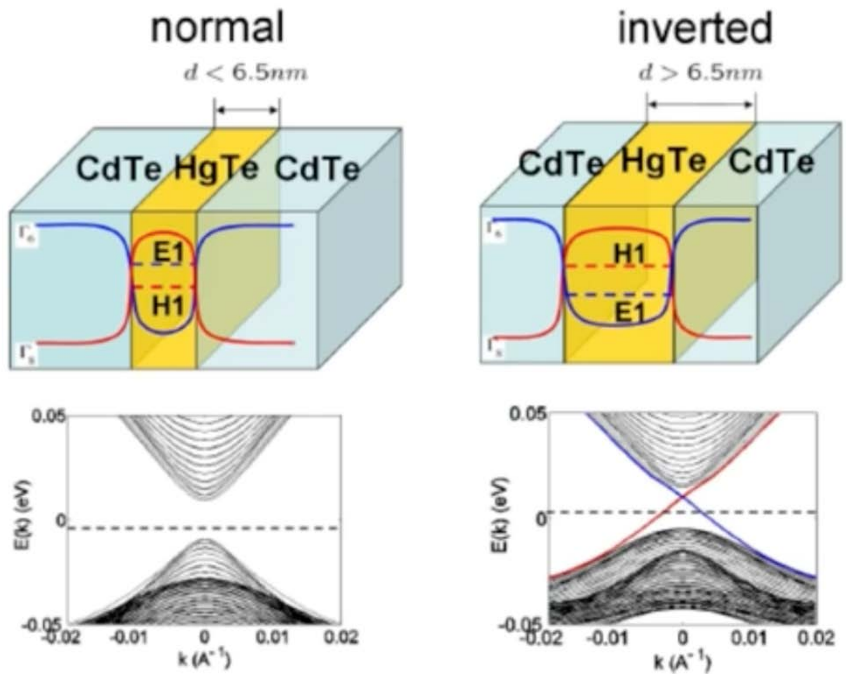
Tight-binding model: P. R. Wallace, (1947)
(nearest neighbor overlap = γ_0)

$$E(\boldsymbol{k}) = E_F \pm \gamma_0 \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$



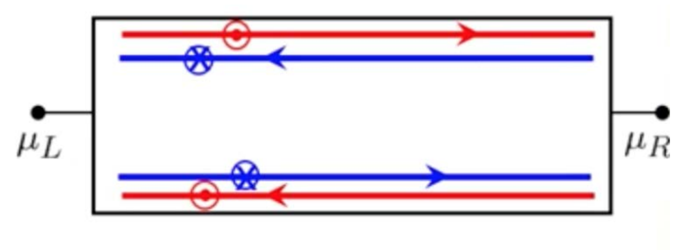


2D TI: Quantum Spin Hall Effect - Experiments

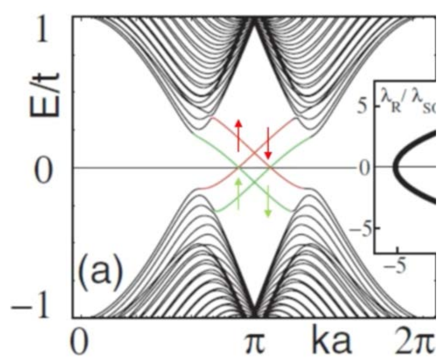


QSHE thought to be ground state of graphene, but SOC too small in graphene

HgTe quantum wells predicted to show QSHE (Bernevig, Zhang 2006)



Perfect (dissipationless) 1D conducting channel



- 1D edge states
- Opposite spins travel in opposite dir.
- TRS
- Two copies of Haldane model
- Topological Z2 invariant: only 2 types of TRS 2D insulators

Koenig et al., Science 318, 766 (2007)

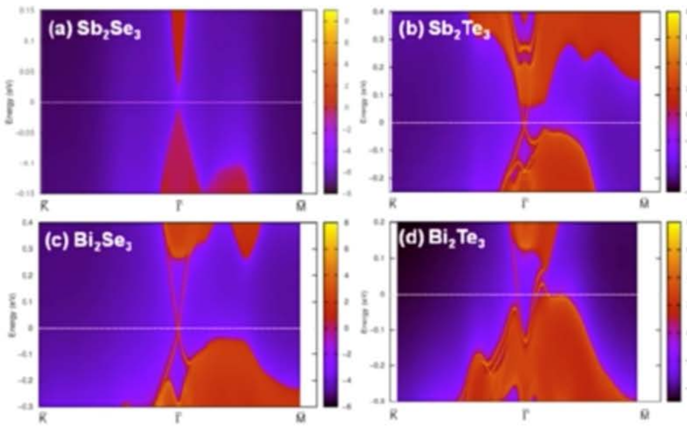
3D TIs: From Theory to Experiments

Theory

Topological insulators in Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 with a single Dirac cone on the surface

Haijun Zhang[1], Chao-Xing Liu[2], Xiao-Liang Qi[3], Xi Dai[1], Zhong Fang[1] and Shou-Cheng Zhang[3]*

DFT calculation

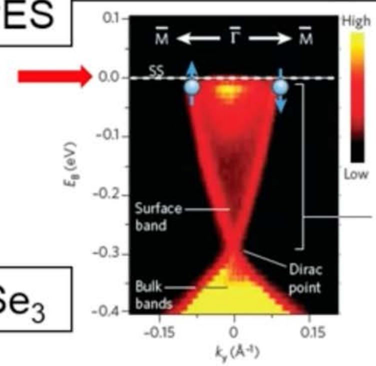


Zhang *et al*., Nature Physics, 5, 438 (2009)

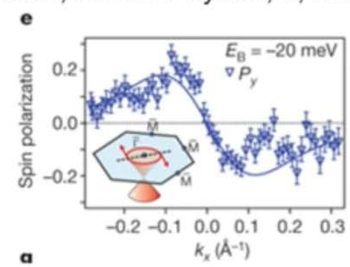
Experiment

ARPES

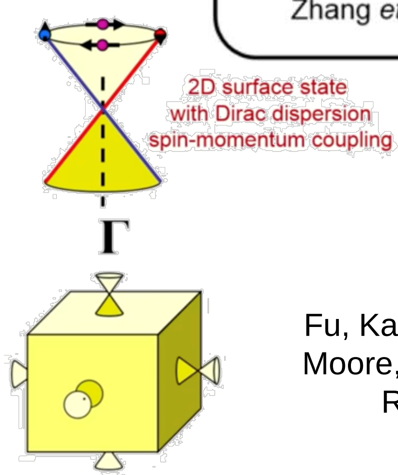
Bi_2Se_3



Xia *et al*., Nature Physics, 5, 398 (2009)

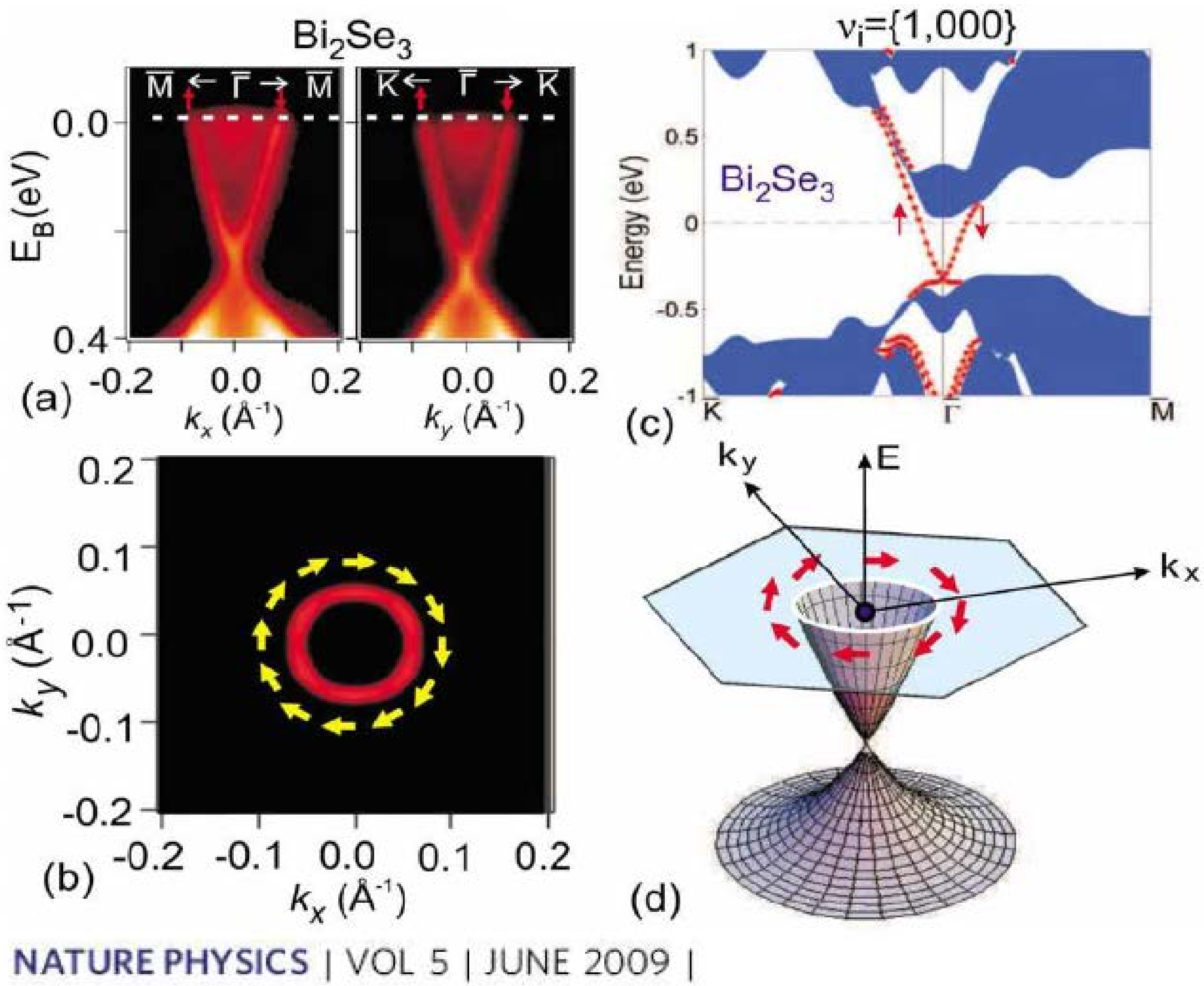


Hsieh, Hasan *et al*., Nature, 460, 1101 (2009)



Fu, Kane, Mele PRL 2005
Moore, Balents PRB 2005
Roy PRB 2009

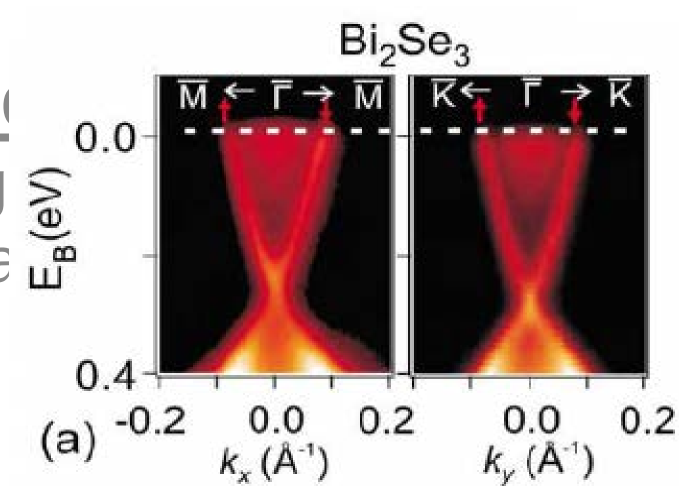
4 Z_2 invariants in 3D:
ν_0; (ν_1, ν_2, ν_3)
ν_0=1: strong TI
ν_0=0, (ν_1,ν_2,ν_3) not all 0:
Weak TI (stacked 2D TIs)



Prediction: Kane, Mele, Fu (PRL 2005, 2007), Bernevig et al. (Science 2006).
Experimental observation: 2D: HgCdTe QWs (König 2007), 3D: $Bi_{1-x}Sb_x$ (Hsieh 2008), Bi_2Se_3 (Xia 2009)

Characterization Techniques:

ARPES, STM, transport, etc. mixed bulk & surface contributions



Re l TI:

insulating e, and high

mea to RT

n-type vs p-type

Goal: Probe *n*- and *p*-Type Materials, With Defects, up to RT

selectivity to bulk vs surface

non-ideal materials, defects

NMR reports on carrier concentration density of states, magnetic order, effective mass, etc.

nanoscale resolution

heterostructures, interfaces

TODAY'S TOPICS

<u>Topological band structures</u>

Topological Insulators

<u>Topological Crystalline Insulators</u>

<u>Dirac Semimetals</u>

TI BULK PROPERTIES

<u>As Probed by Conventional SS-NMR</u>

Bulk Defects

Phase Separation

Electronic Homogeneity

Carrier conc. & Type, *p*-to-*n* Transition

Band Inversion

Adv. Electr. Mater. 1, 1500117 (2015); APL Materials 3, 083601 (2015); Phys. Rev. B 90, 125201 (2014); Adv. Func. Mater. 24, 1519-1528 (2014); J. Phys. Chem. C 117, 8959-8967 (2013); J. Phys. Chem. C 116, 17300-17305 (2013)

E-N Hyperfine Interaction

$$H_D = -2\mu_B\gamma_n\hbar\mathbf{I}\cdot\left[\frac{\mathbf{1}}{r^3} - \frac{3\mathbf{rr}}{r^5}\right]\cdot\mathbf{S}$$

$$H_O = -\gamma_n\hbar\frac{e}{mc}\frac{\mathbf{I}\cdot(\mathbf{r}\times\mathbf{p})}{r^3}$$

$$H = H_Z + H_Q + \{H_F + H_D + H_O\}$$

$$\|H_Z\| \gg \|H_Q\| \gg \|H_D\|, \|H_O\|$$

$$H_F = 2\left(\frac{8\pi}{3}\right)\mu_B\gamma_n\hbar\mathbf{I}\cdot\mathbf{S}\delta(\mathbf{r})$$

$$H_Z = -\gamma\hbar B_0\sum_i I_{z,i}$$

$$H_Q = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - \vec{I}^2 + \frac{1}{2}\eta\left(I_+^2 + I_-^2\right)\right]$$

Spin dynamics

$$\frac{1}{T_1} = \left(64\frac{\pi^3}{9}\right)\gamma_e^2\gamma_{Li}^2\hbar^3\langle|\Psi_k(0)|^2|\Psi_{k'}(0)|^2\rangle_F N_{s,p}(E_F)^2 k_B T$$

$$\frac{1}{T_1} \propto (m_e^*)^2 n_e^{\frac{2}{3}} kT$$

Fermi-Dirac

$$\frac{1}{T_1} \propto (m_e^*)^{\frac{3}{2}} n_e (kT)^{\frac{1}{2}}$$

Maxwell-Boltzmann

Knight Shift

$$K = \zeta\left(\frac{8\pi}{3}\right)\gamma_e^2 h^2 \langle|u_{k(0)}|^2\rangle_{E_0}\left(\frac{n_e}{kT}\right)$$

Orbital Hyperfine Interaction (TI)

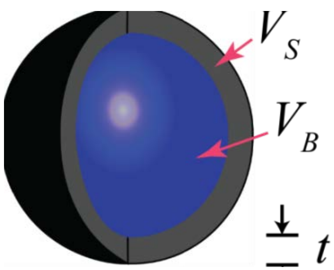
$$H_O \sim \frac{\mathbf{I} \cdot (\mathbf{r} \times \mathbf{p})}{r^3} \qquad H_O^{(TI)} \sim \frac{\mathbf{I} \cdot (\mathbf{r} \times v_F \boldsymbol{\sigma})}{r^3}$$

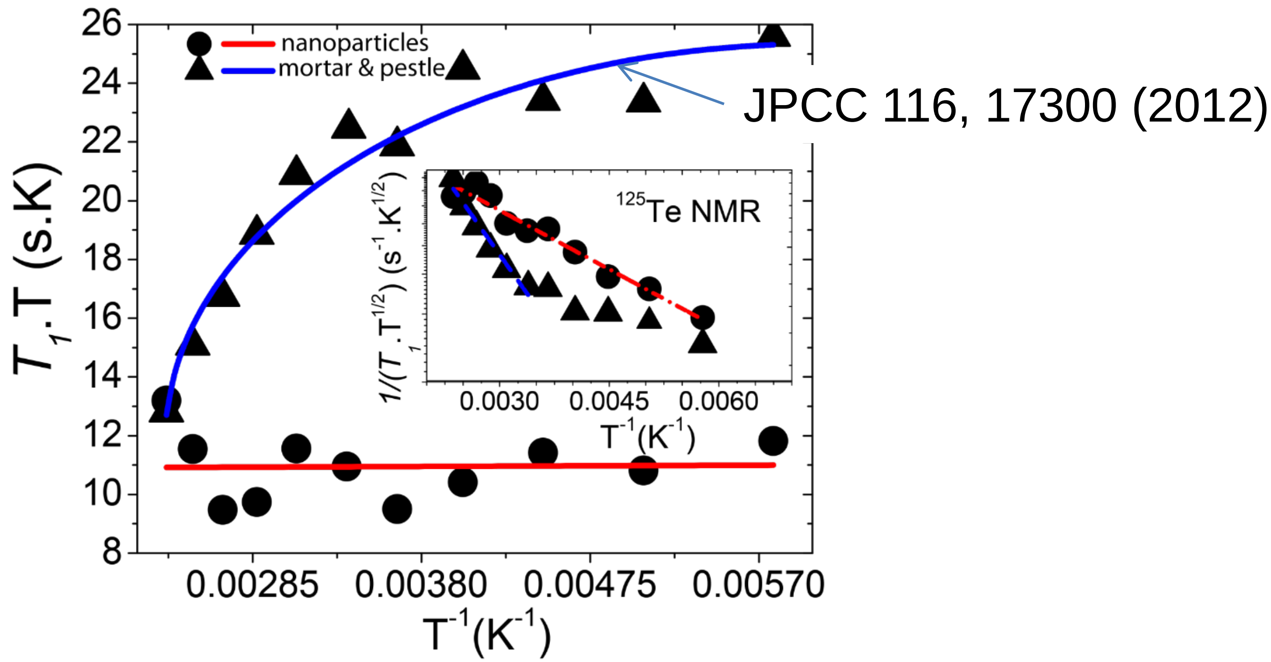
$v_F \sim 5\ 10^5$ m/s or ~0.7 eV
vs 10^{-6} eV for usual HFI

(nucleus interacts with orbital motion of Dirac electron)

KORRINGA LAW IN Bi_2Te_3

<u>First Time Observed in a TI</u>

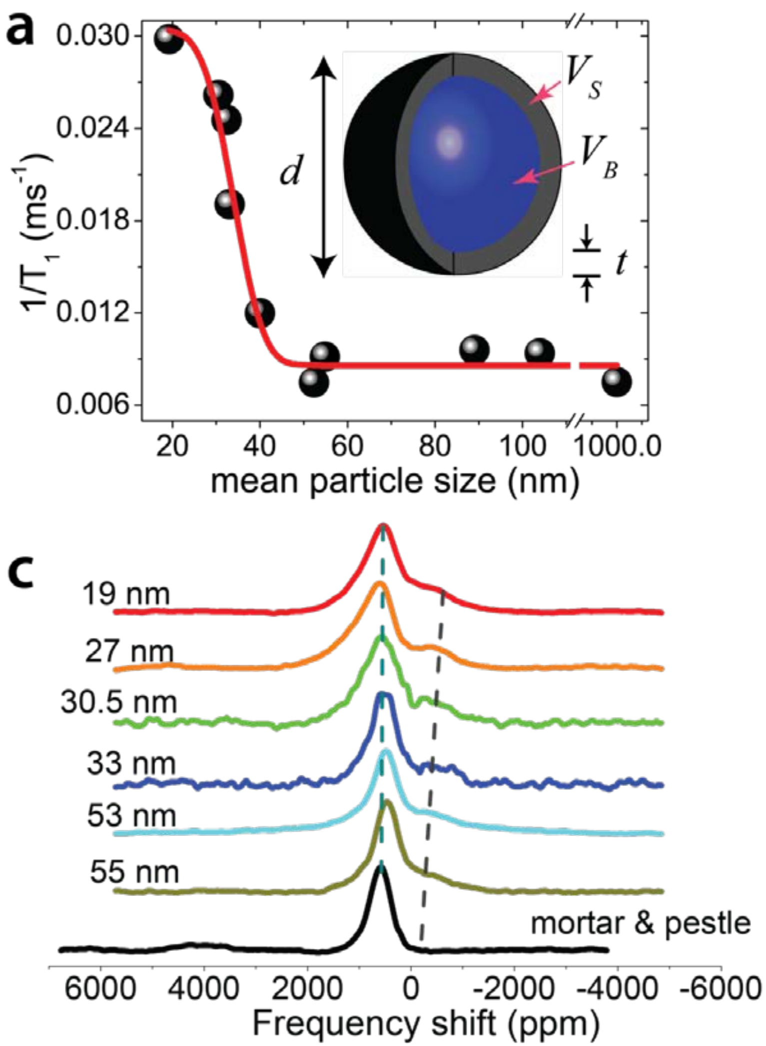




D. Koumoulis, et al., Phys. Rev. Lett. 110, 026602 (2013)

NEGATIVE KNIGHT SHIFT

First Time Observed in a TI



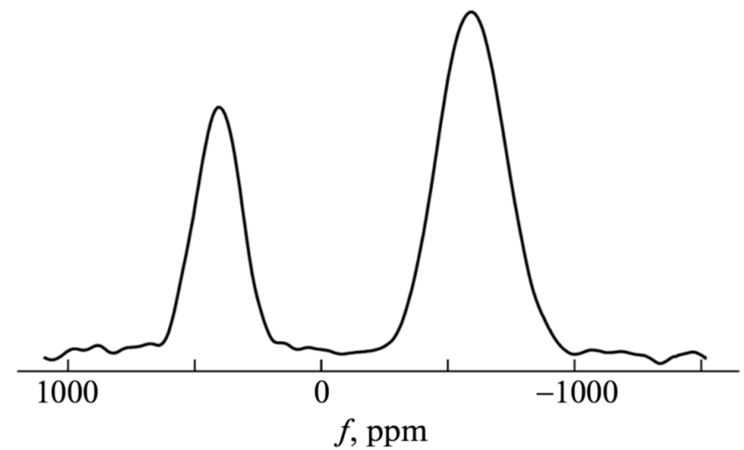


Fig. 1. ^{125}Te NMR spectrum of Bi_2Te_3 single crystal at room temperature. The *c* axis of the crystal is directed along the external magnetic field.

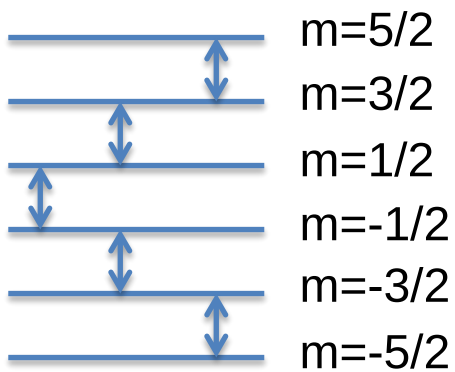
Podorozhkin, et al., Phys. Solid State 57, 1741 (2015)

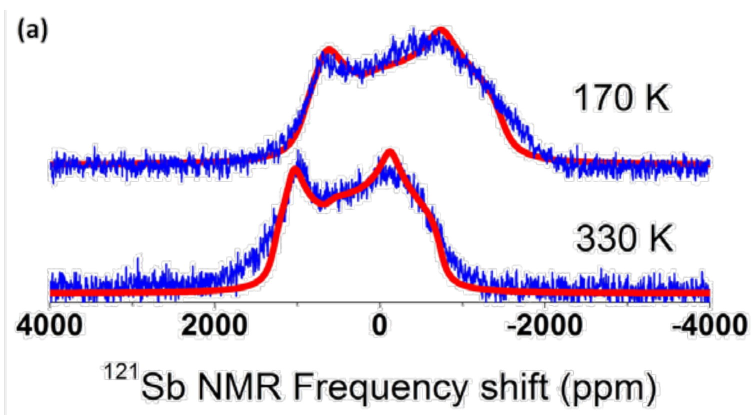
D. Koumoulis, et al., Phys. Rev. Lett. 110, 026602 (2013)

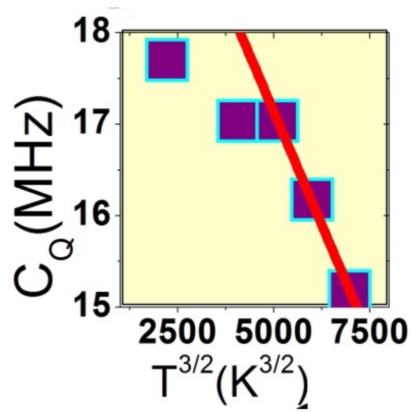
Nuclear Quadrupolar Central Transition

^{121}Sb nuclei
(I=5/2)

$$H_Q = \mathbf{I} \cdot \overleftrightarrow{Q} \cdot \mathbf{I}$$







^{121}Sb vs T for Sb_2Te_3

http://www.pnas.org/content/112/28/E3645/suppl/DCSupplemental

Isotopic Ratio & Korringa Law

magnetic relaxation mechanism

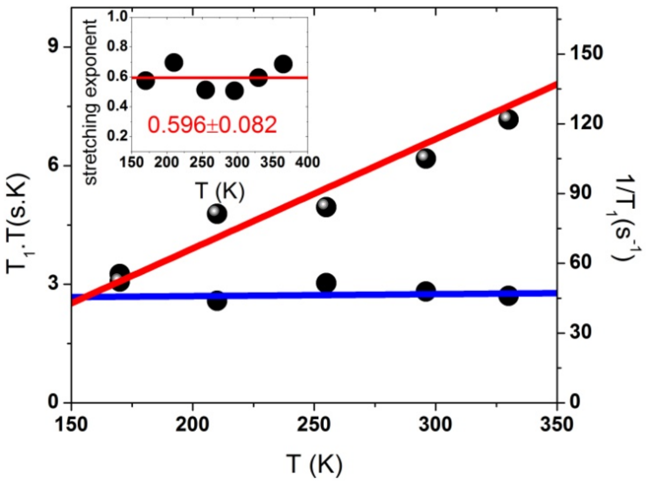
^{121}Sb nuclei (I=5/2)

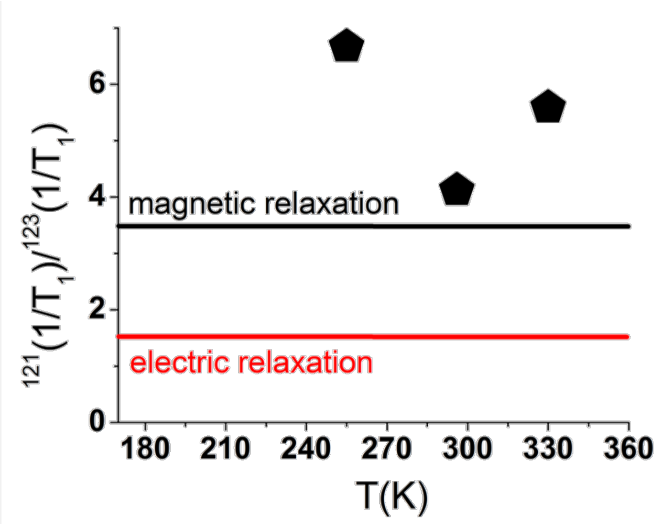
$$\frac{121_{\left(\frac{1}{T_1}\right)}}{123_{\left(\frac{1}{T_1}\right)}} = \frac{121_{\gamma_n^2}}{123_{\gamma_n^2}} = 3.41$$

^{123}Sb nuclei (I=7/2)

electric relaxation mechanism

$$\frac{121_{\left(\frac{1}{T_1}\right)}}{123_{\left(\frac{1}{T_1}\right)}} = \frac{(121_Q)^2 \times \frac{(2I+3)}{I^2(2I+1)}}{(123_Q)^2 \times \frac{(2I+3)}{I^2(2I+1)}} = 1.44$$

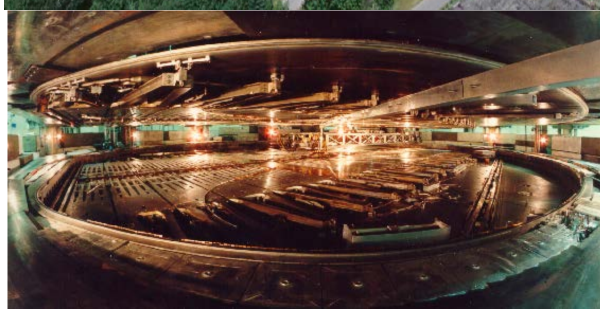


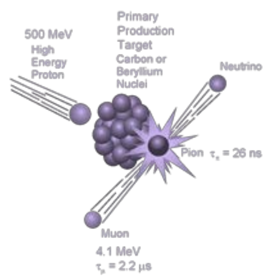


http://www.pnas.org/content/112/28/E3645/suppl/DCSupplemental

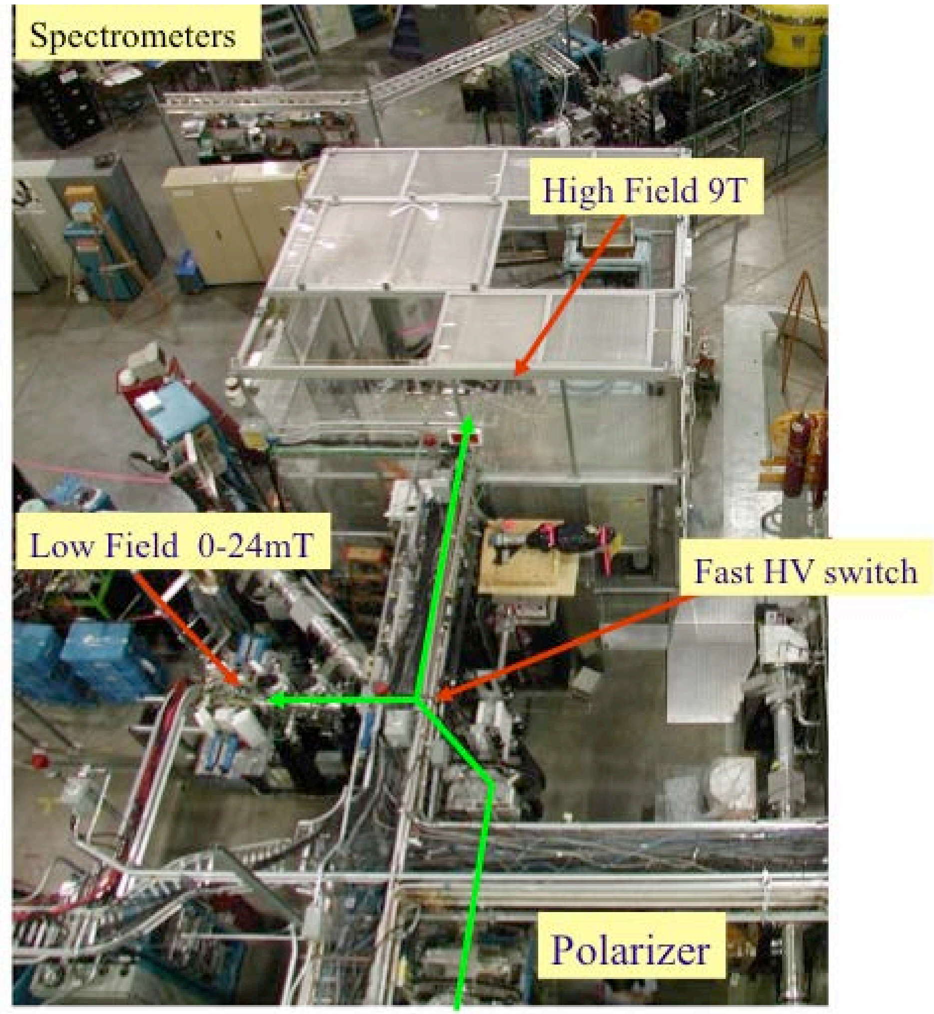
βNMR STUDIES

@ ISAC-I Facility, TRIUMF

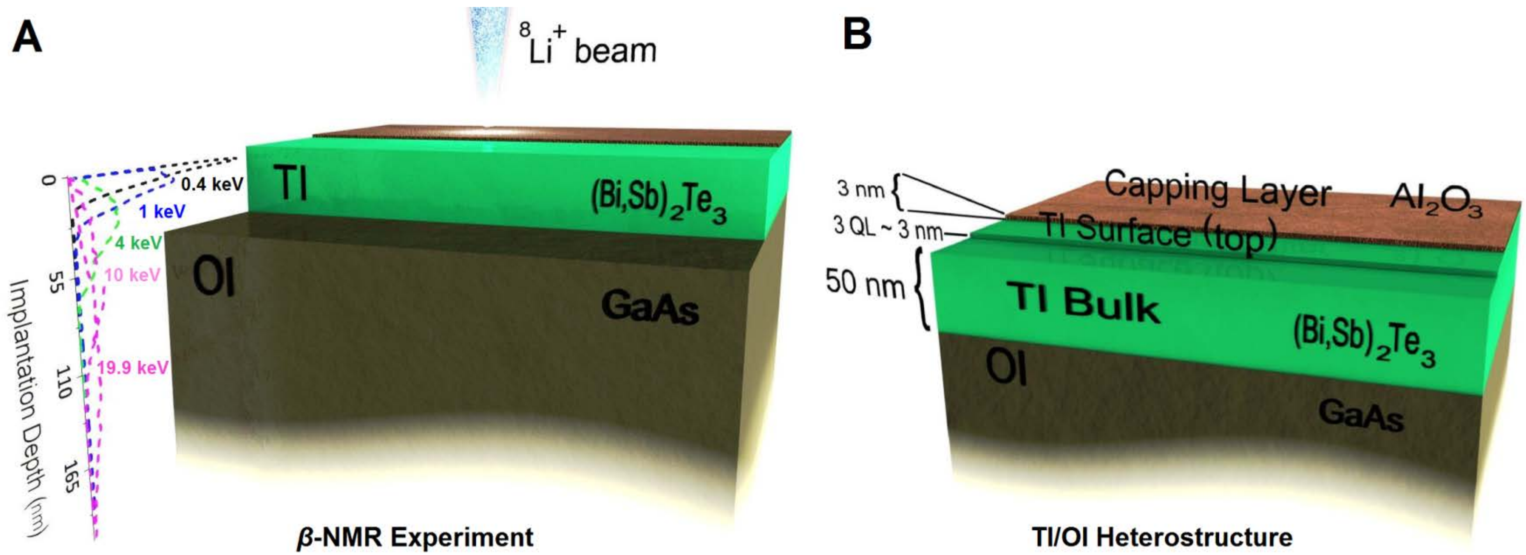




	NMR	μSR	β-NMR
Polarization	<0.01	>0.8	
detection method	electronic pickup	anisotropic β decay	
Sensitivity	10^{17} spins	10^{7} spins	
T_1 range (s)	$10^{-5} – 10^{2}$	$10^{-8} – 10^{-4}$	$10^{-3} – 10^{3}$
range	N/A	0.5 mm	10 Å –3000 Å*
Applied field	high	any	small-high



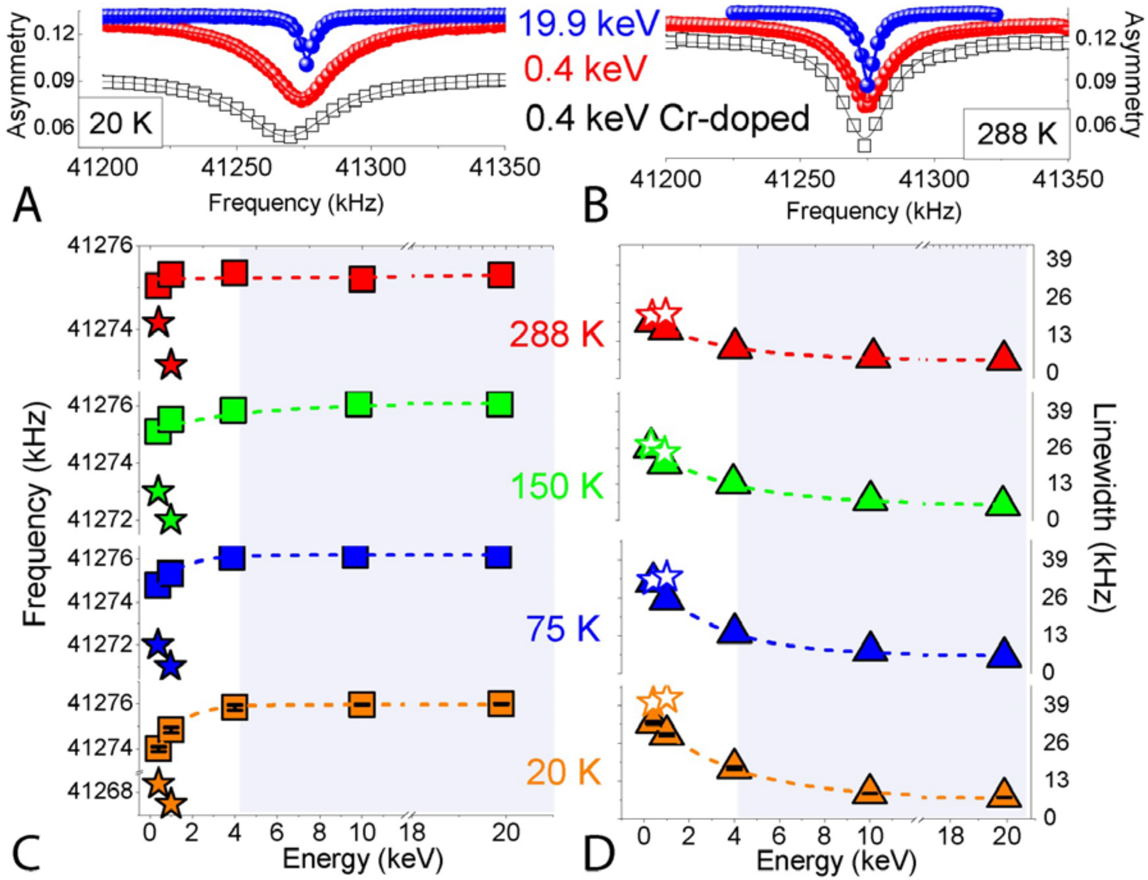
M1352: TI/OI Thin-Film Heterostructure



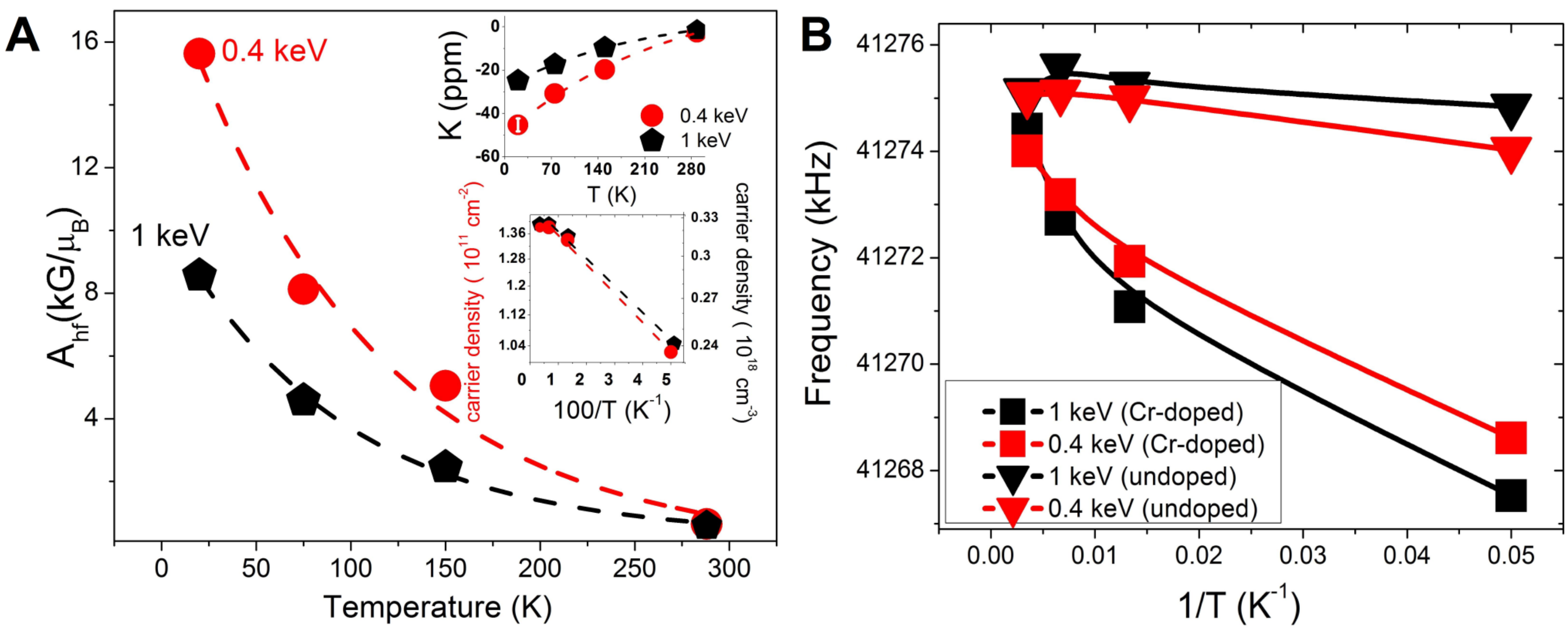
0.4 keV, 50% signal originates from TI surface, d=4 3 nm
1 keV , 80% originates from TI bulk

Knight Shift Measures Carrier Density, s-o Mixing, Density of States @ E_F

$$K = \frac{4\pi}{3} g . g^* . \mu_B^2 . \langle |u_k(0)|^2 \rangle_{E_0} \rho(E_F) \qquad (\cos^2\theta^+) \langle R | \Delta(\vec{r}) | R \rangle$$

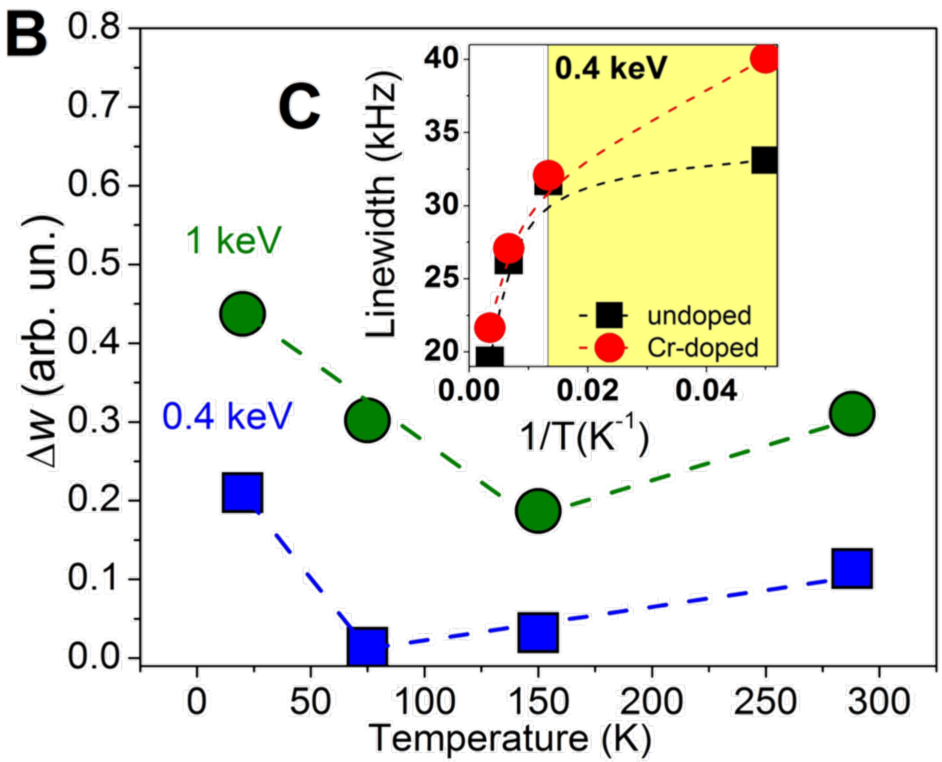


M1352: Knight Shift, Hyperfine Constant, Local Carrier Concentration



D. Koumoulis, et al., PNAS 112, E3645-E3650 (2015)

Depth-Resolved Magnetic Properties



$$\Delta w = \frac{W_{CrTI} - W_{TI}}{W_{TI}}$$

$$\frac{W_{CrTI} - W_{TI}}{W_{TI}} = \left(\frac{Jp^2C}{3gk_B}\right) \cdot \frac{1}{T} + D$$

p effective number of Bohr magnetons
C atomic fraction of paramagnetic atoms
D temperature independent term
g electron *g*-factor
J effective *s*-*d* exchange integral

D. Koumoulis, et al., PNAS 112, E3645-E3650 (2015)

Nanoscale Findings From Depth Profiling

when going from the bulk to the surface, across a ~10 nm thick layer…

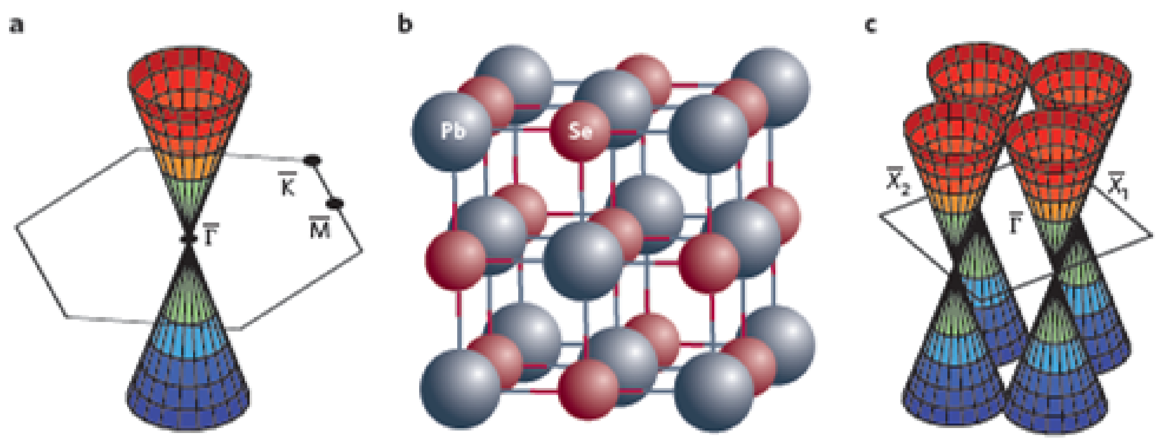
$$
\begin{aligned}
T_c^{surface} &= 0.5 \cdot T_c^{bulk} \\
J^{surface} &= 0.9 \cdot J^{bulk} \\
n_e^{surface} &= 2 \cdot n_e^{bulk} \\
A_{hf}^{surface} &= 2 \cdot A_{hf}^{bulk}
\end{aligned}
$$

J: effective *s-d* exchange integral

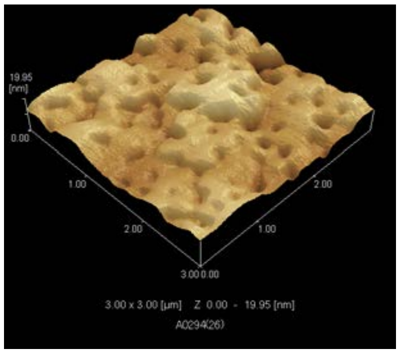
D. Koumoulis, et al., PNAS 112, E3645-E3650 (2015)

TOPOLOGICAL CRYSTALLINE INSULATORS

<u>TCIs Have Even Number Of Dirac Cones</u>



$Pb_{1-x}Sn_xSe$



crystalline symmetry replaces time-reversal symmetry

surface states protected by crystal mirror symmetry

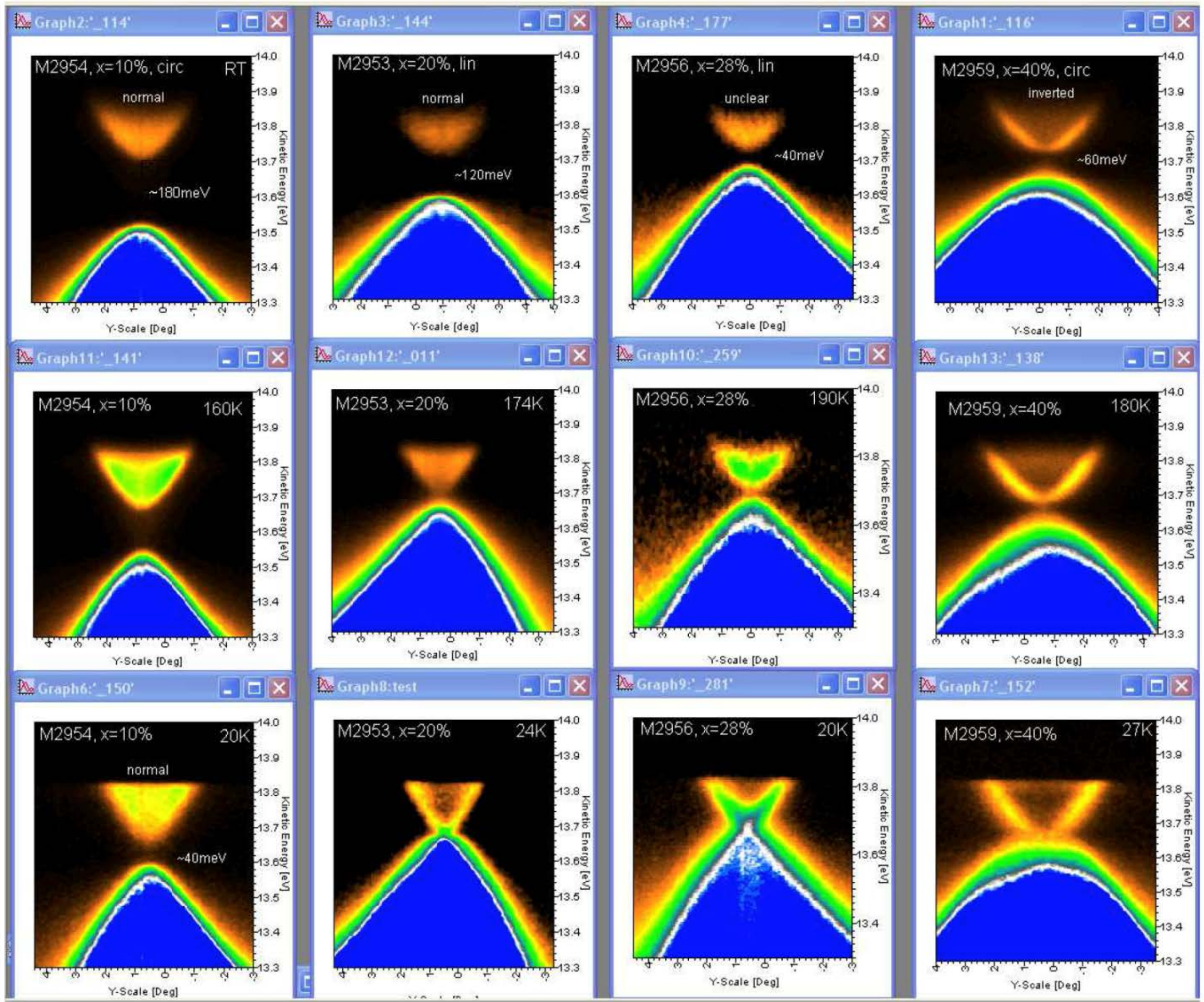
only on crystal faces perpendicular to the mirror planes

L. Fu, Phys. Rev. Lett. 106, 106802 (2011); T.H. Hsieh, et al., Nature Comm. 3, 982 (2012).

ARPES of $Pb_{1-x}Sn_xSe$, x=10-40%

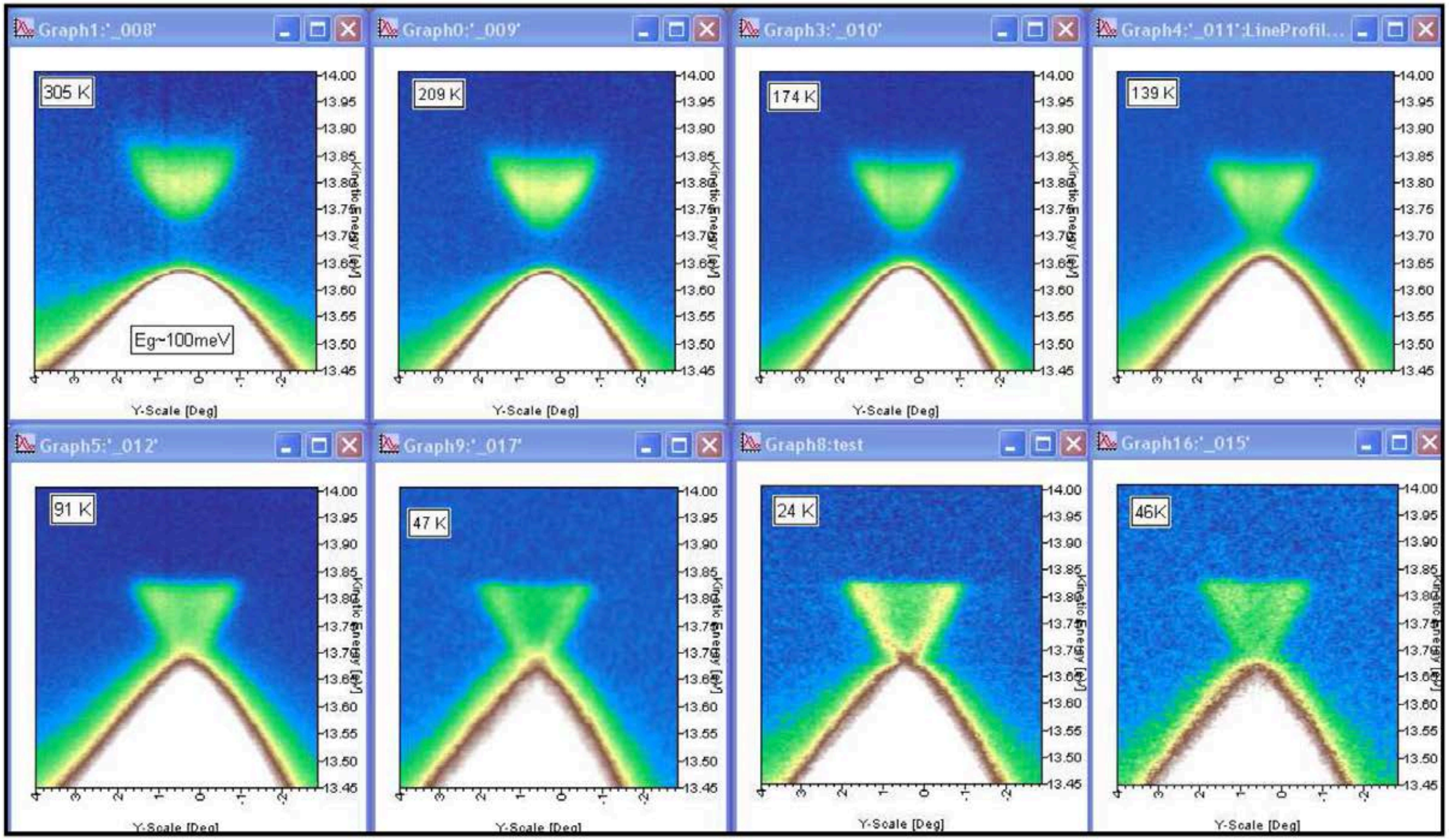
At room temperature (upper row), at ~180K (middle) and at 20K (lower row)

vs T



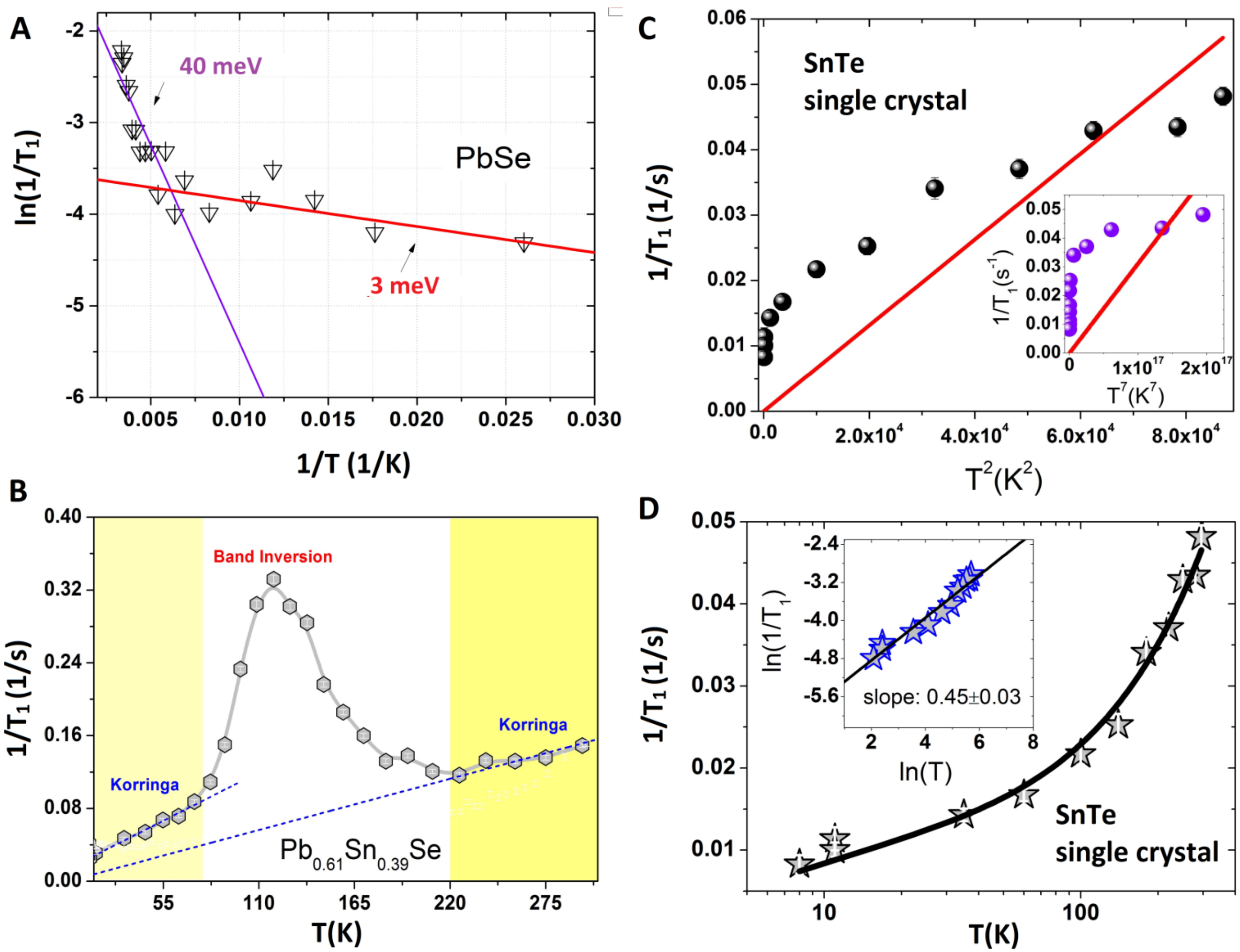
vs doping (x=0.1, 0.2, 0.3, 0.4)

CD vs T, $Pb_{1-x}Sn_xSe$, x=20%



Recall that $$\frac{1}{T_1} \propto N_{s,p}(E_F)^2$$

Spin Dynamics and BI



$Pb_{0.61}Sn_{0.39}Se$ @ 130K, drop in resistivity

Ferroelectricity:

Van Kranendon & Walker (1968)

$$\frac{1}{T_1} \propto T^2 \text{ for } T \geq \Theta_D$$

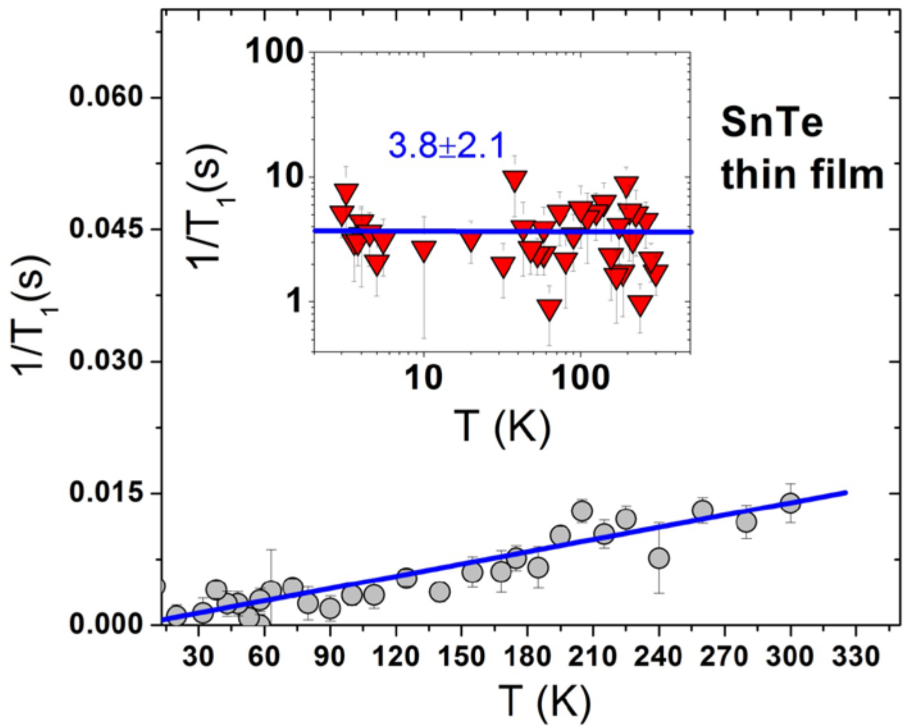
$$\frac{1}{T_1} \propto T^7 \text{ for } T \leq \Theta_D$$

$\Theta_D \sim 150$ K SnTe

$1/T_1$ expected to change at $T_c \sim 100$ K (critical slowing of the soft mode)

$$\frac{1}{T_1 \cdot T} = \frac{1}{T_{1K} \cdot T} + C \cdot T \cdot e^{-\frac{\Delta}{k_B T}}$$

Surface State like Conductive Metal

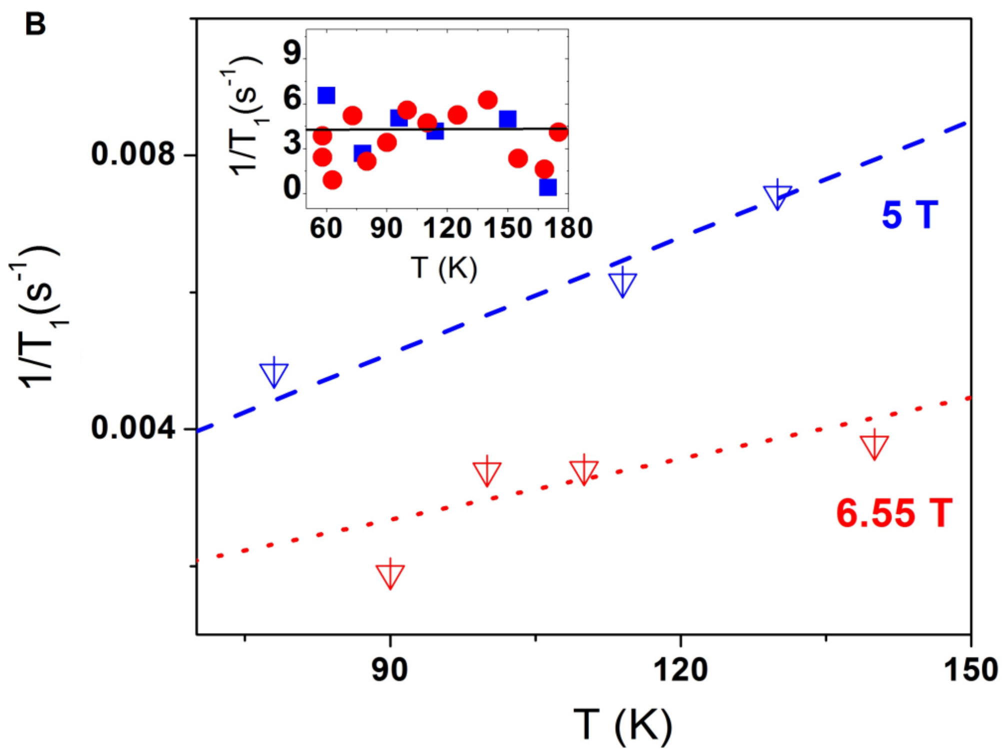


$1/T_1$.T~0.98 -> highly conductive state (non-interacting carriers, no electron-electron correlations)

SnTe surface is more metallic than Ag or Au

Metallicity hard to detect via volume-averaged readouts

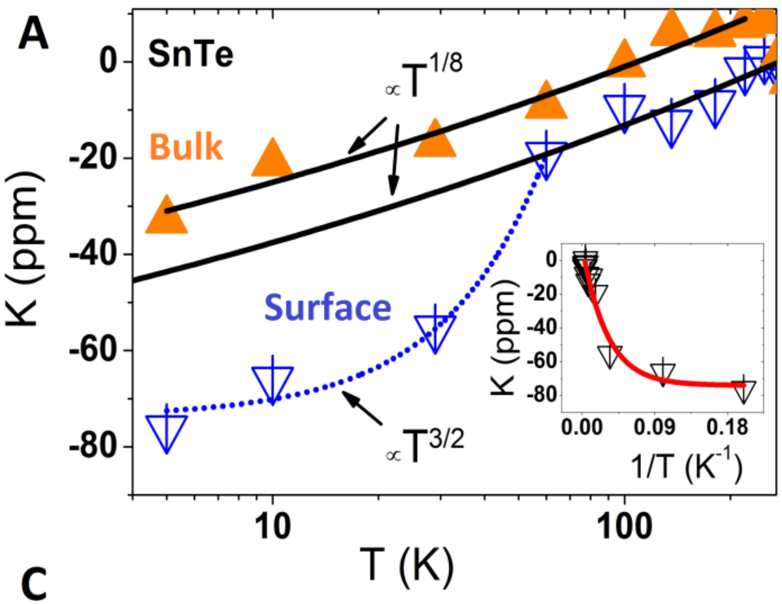
Field-Depending Korringa Process

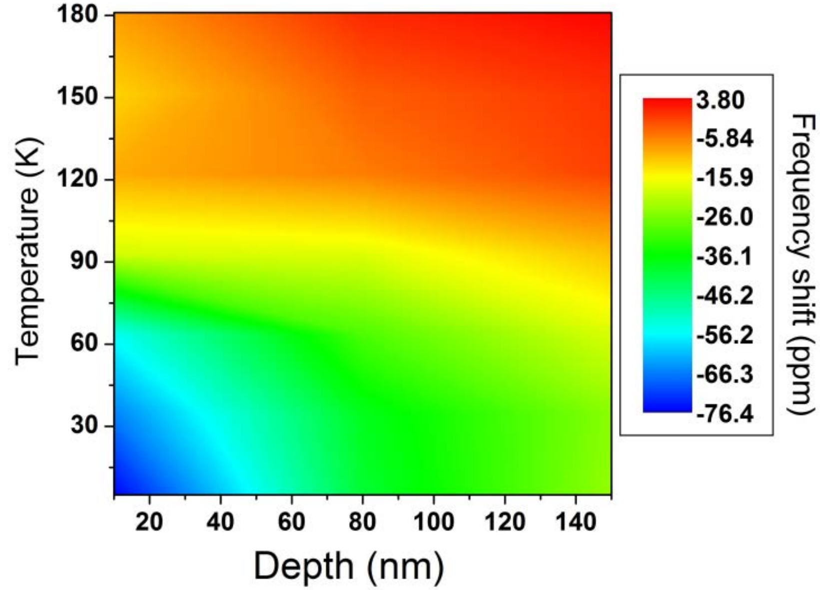


Field dependence also observed in various quantum Hall systems.

Knight Shift @ Surface Reveal Gapless Semiconductor

$$K = B \cdot T^n + D$$

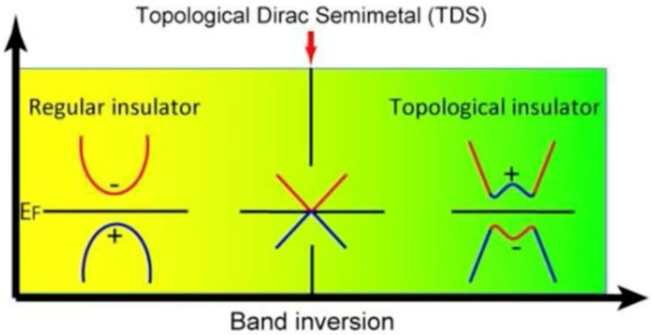




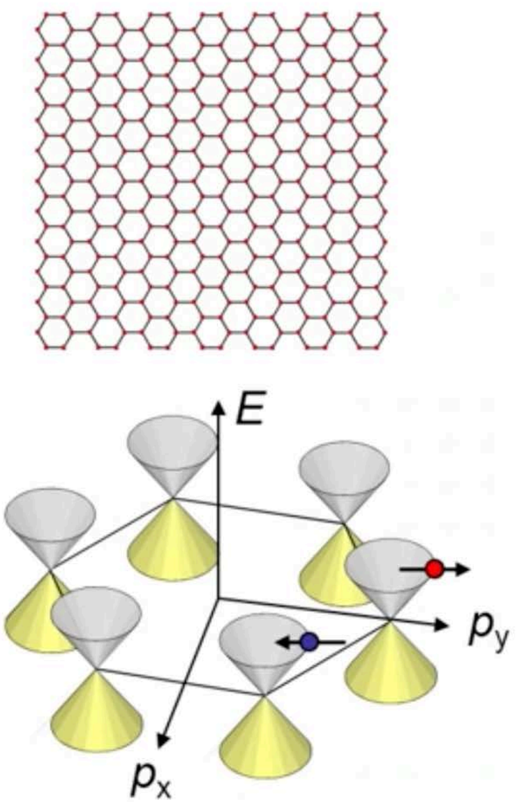
$1/T^{3/2}$ law typical of gapless semiconductors
(Tsidilkovski 1997, Zhang 2015)
sub-linear power law (<1) due to presence of defects and disorder

Topological Dirac Semimetals

TDS lie at a quantum critical point between trivial insulator and TI



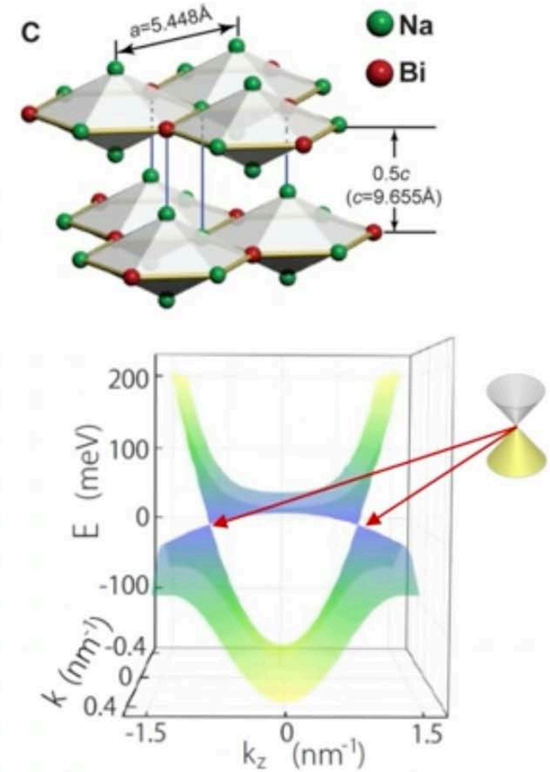
Graphene (2D)



$$H = v_F(\boldsymbol{\sigma} \cdot \mathbf{p})$$

Na_3Bi (3D)

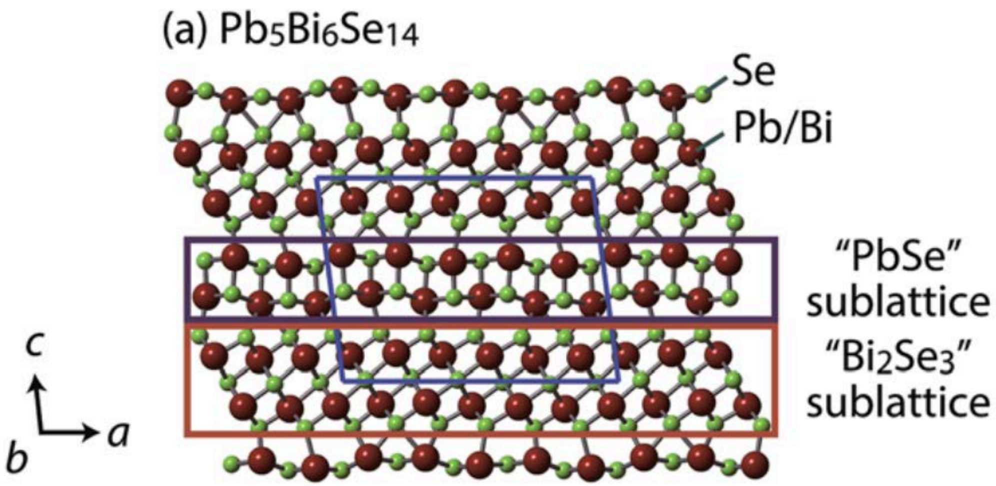
(3D topological Dirac semimetal)



$$H = v_F(\boldsymbol{\sigma} \cdot \mathbf{p})$$

also
Cd_3As_2
$ZrTe_5$(?)
Others?

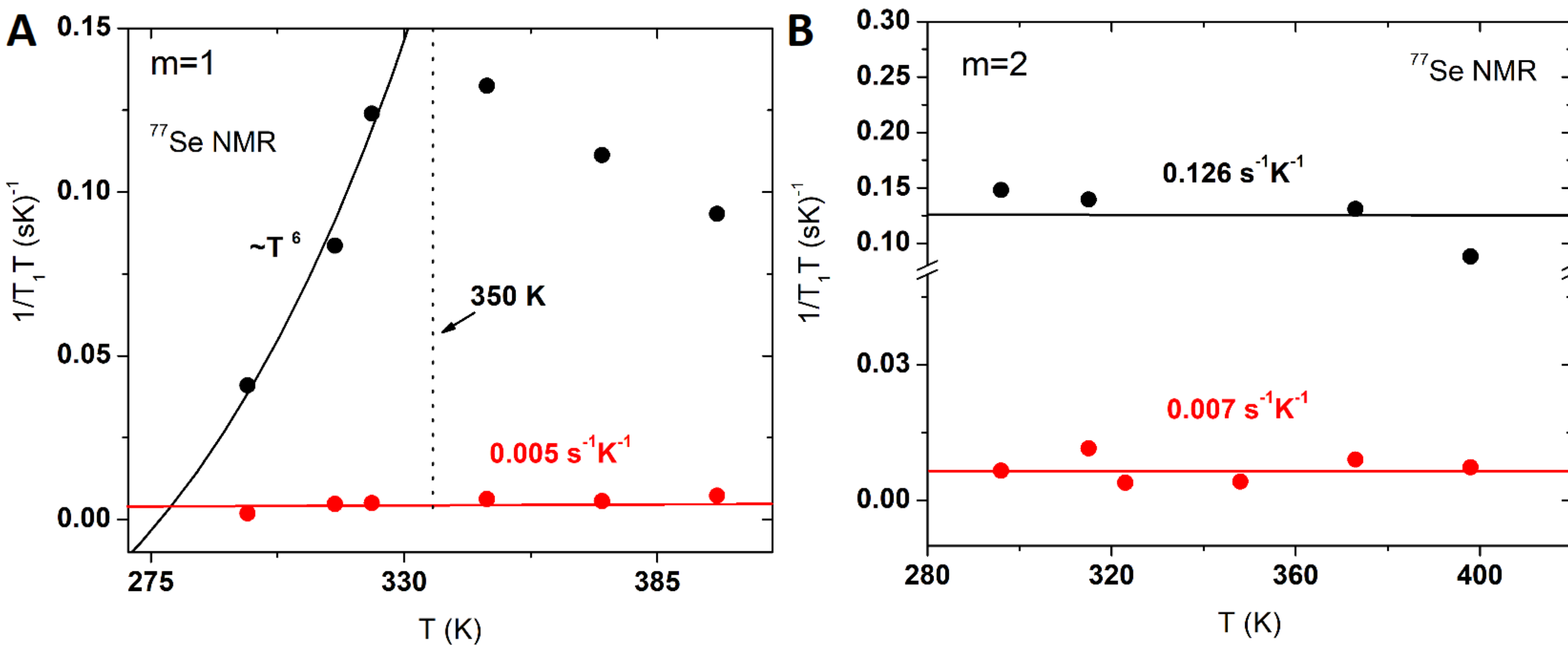
Evolution of non-trivial Fermi Surface Features in the Band Structures of $Pb_5Bi_6Se_{14}$ and $Pb_5Bi_{12}Se_{23}$



$(PbSe)_5(Bi_2Se_3)_{3m}$

m=1 $Pb_5Bi_6Se_{14}$ semiconducting

m=2 $Pb_5Bi_{12}Se_{23}$ semimetallic



A
m=1
77Se NMR
~T 6
350 K
0.005 s-1K-1
1/T1T (sK)-1
T (K)
0.15
0.10
0.05
0.00
275
330
385
B
m=2
77Se NMR
0.126 s-1K-1
0.007 s-1K-1
1/T1T (sK)-1
T (K)
0.30
0.25
0.20
0.15
0.10
0.03
0.00
280
320
360
400

SUMMARY

Topological States

TI bulk & surface States near RT, p-type materials, studies of materials with high defect content

TCIs slightly more complicated because of the band inversion vs T and x; no ferroelectric transition in SnTe

Contributors:

D. Koumoulis, J.P. Scheifers, R. Touzani, B.P.T. Fokwa, R.E. Taylor, K.L Wang, L. He, X. Kou, D. King, F. Alkan, C. Dybowski (U Del.), G.D. Morris (TRIUMF), G.A. Fiete (UT Austin), M.G. Kanatzidis (NWU), Thomas Chasapis (NWU), G. Springholz (Linz), R. Akiyama, S. Ishikawa, S. Kuroda (Univ. of Tsukuba)

For More Info See:

Adv. Electr. Mater. 1, 1500117 (2015); Proc. Natl. Acad. Sci. USA 112, E3645-E3650 (2015); APL Materials 3, 083601 (2015); Phys. Rev. B 90, 125201 (2014); Adv. Func. Mater. 24, 1519-1528 (2014); J. Phys. Chem. C 117, 8959-8967 (2013); Phys. Rev. Lett. 110, 026602 (2013); J. Phys. Chem. C 116, 17300-17305 (2013)

ACKNOWLEDGMENTS