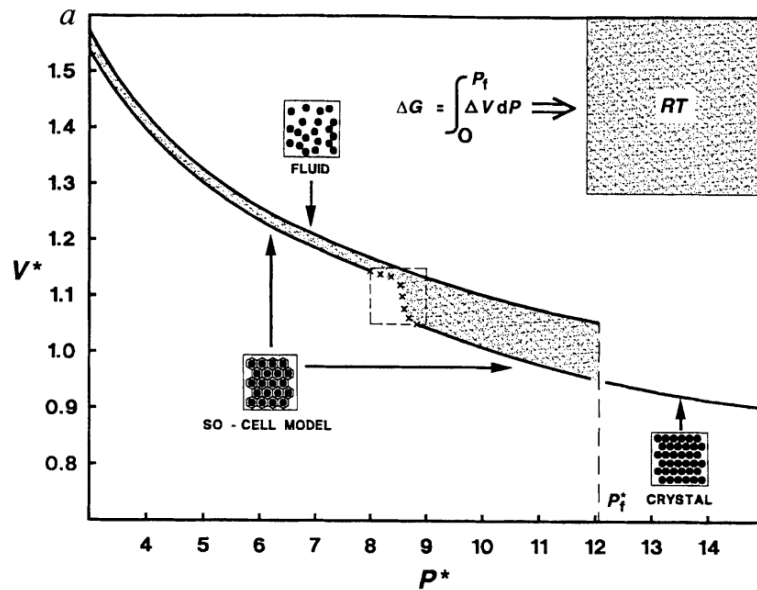
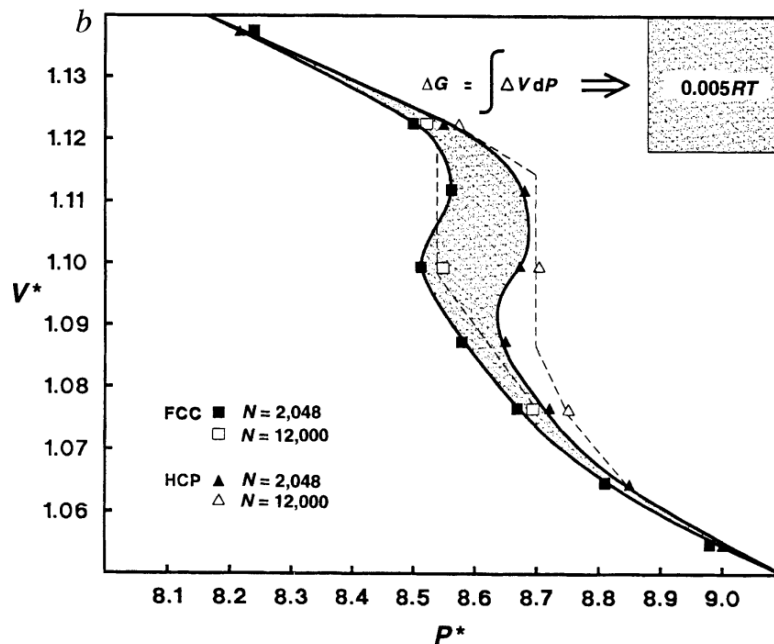


Close packings: *fcc*, *hcp*, diamond, zinc blende, wurtzite, SiC, semiconductors



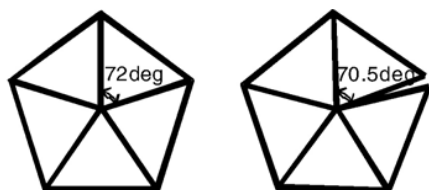
Hard spheres: *fcc* is slightly stabilized by entropy over *hcp*, by $0.005 R$ for all temperatures up to the melting point.

L. V. Woodcock, *Nature* **385** (1997) 141.



Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors

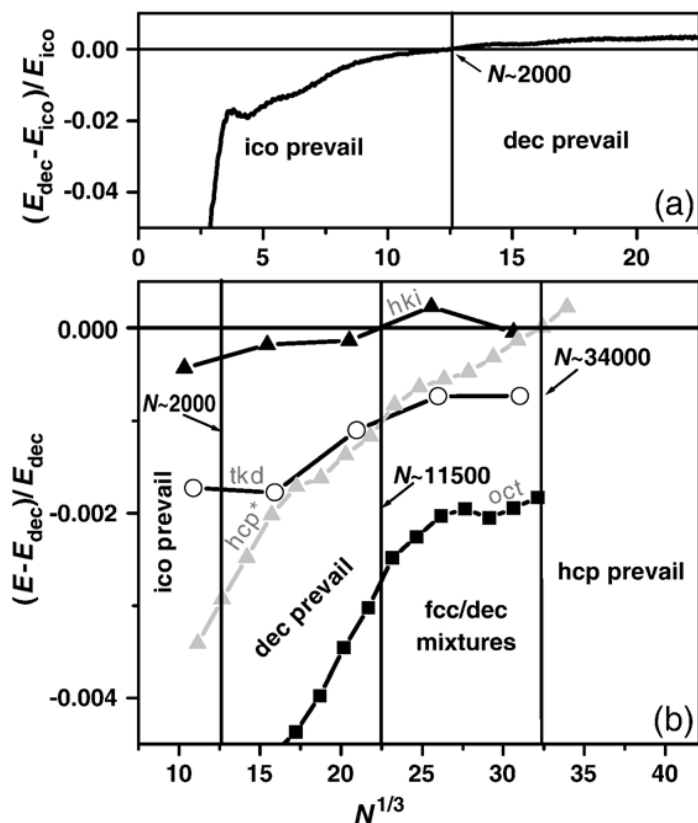
The *hcp-fcc* dilemma: Why is *fcc* more frequent than *hcp* ? [25% of elements are *fcc* and 20% are *hcp*.



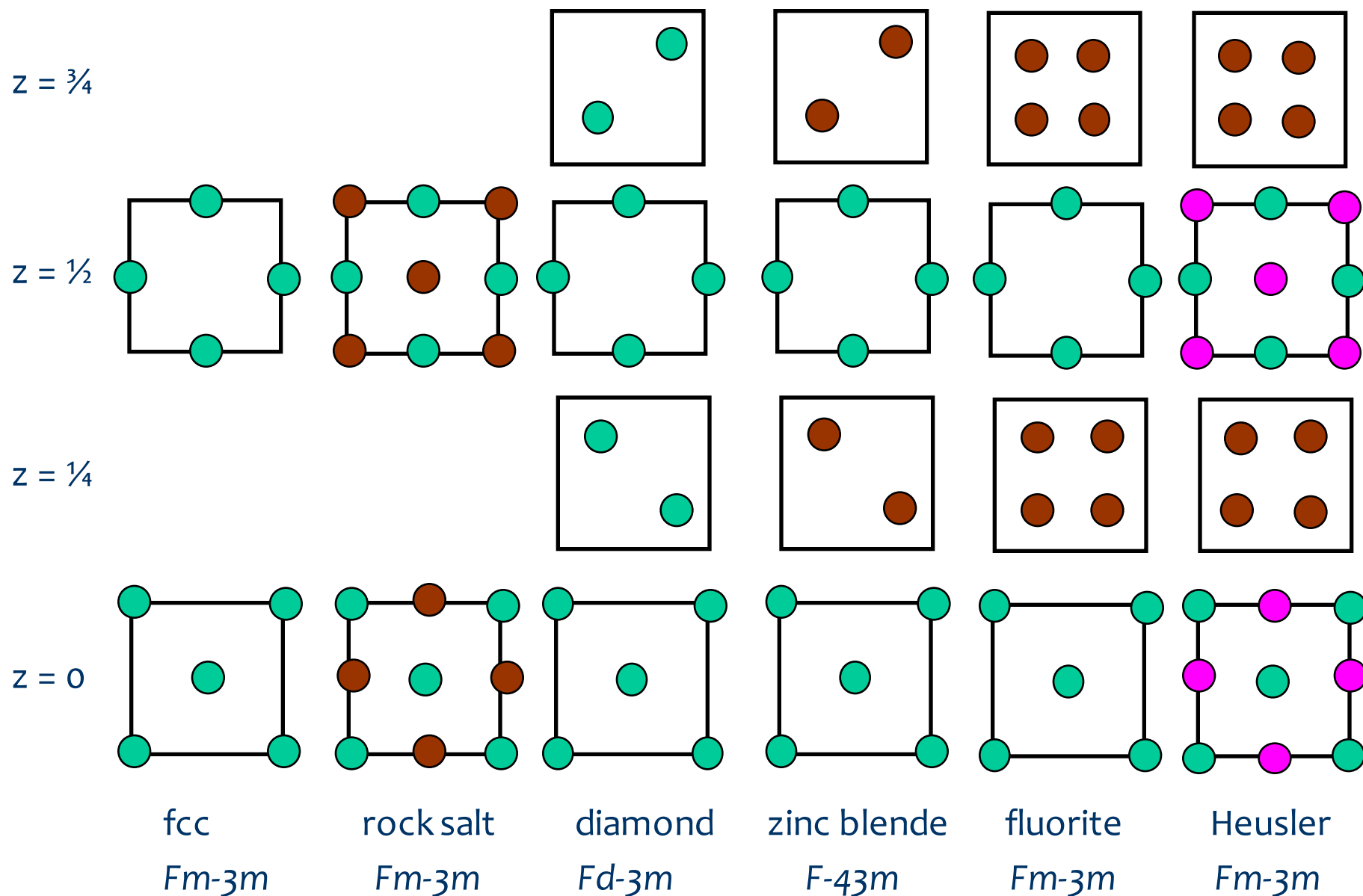
N. V. Krainyukova, The “crystal structure problem” in noble gas nanoclusters, *Thin Solid Films*, **515** (2006) 1658–1663.

Calculations of the energetics of multiply twinned particles (MTPs) such as icosahedra and decahedra with fivefold symmetry as well as facecentered cubic (fcc) and hexagonal close-packed (hcp) particles in the size interval from 13 up to ~45,000 atoms were made applying Lennard-Jones potentials.

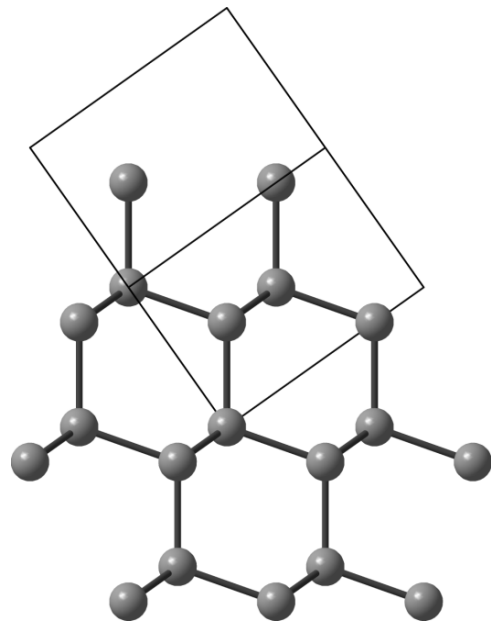
For the cluster size N from minimal up to $N \sim 2000$ atoms the binding energy is highest for icosahedra, in the size interval from 2000 up to $\sim 11,500$ atoms decahedra prevail, above $N \sim 11,500$ atoms decahedra and optimized fcc clusters were found to alternate. The hcp structure was revealed to become favorable above $N \sim 34,000$ atoms. Thus, hcp clusters can attain their preference with respect to MTPs (comprising fcc fragments) and optimized fcc clusters only for very large sizes



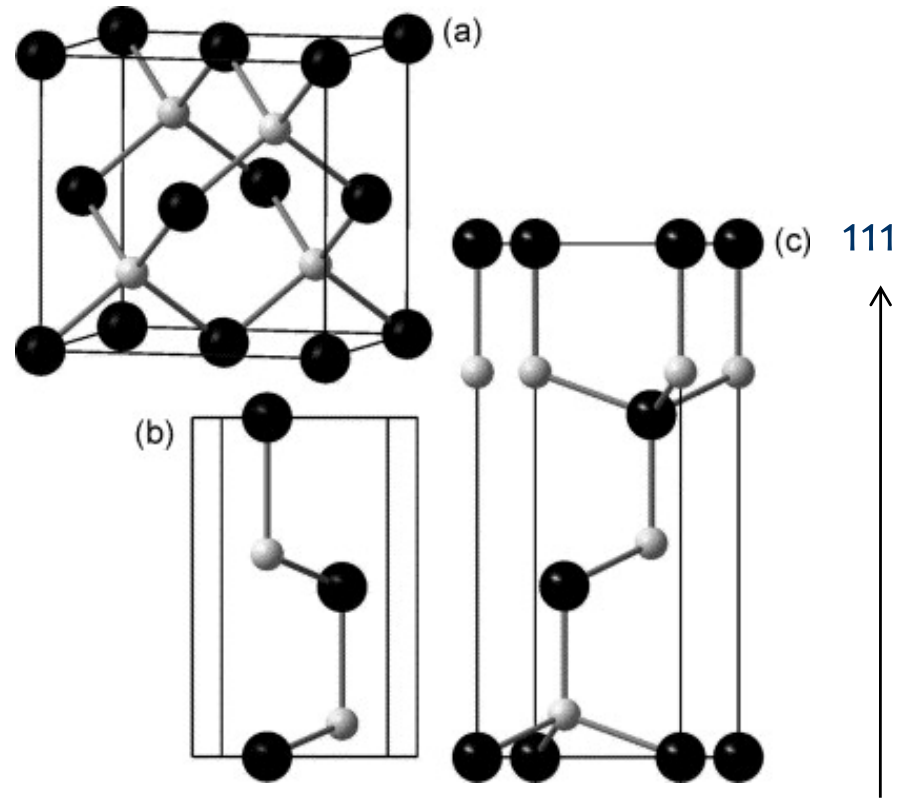
Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors



Class 2: *fcc*, *hcp*, diamond, zinc blende, wurtzite, SiC, semiconductors



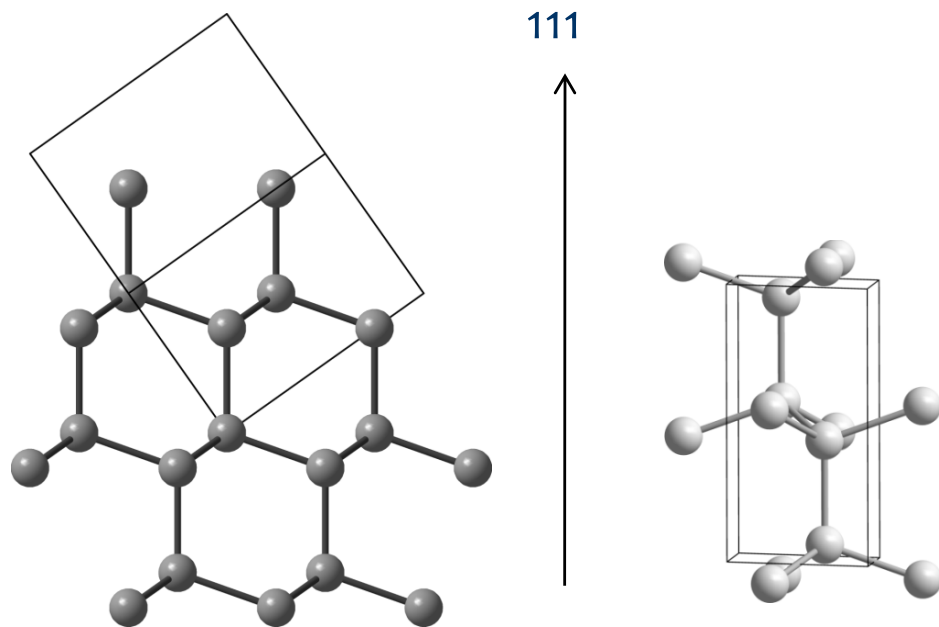
Diamond



Wurtzite and zinc blende

P63mc and *R3m/F-43m*
2H and *3R*

Class 2: *fcc*, *hcp*, diamond, zinc blende, wurtzite, SiC, semiconductors



Diamond

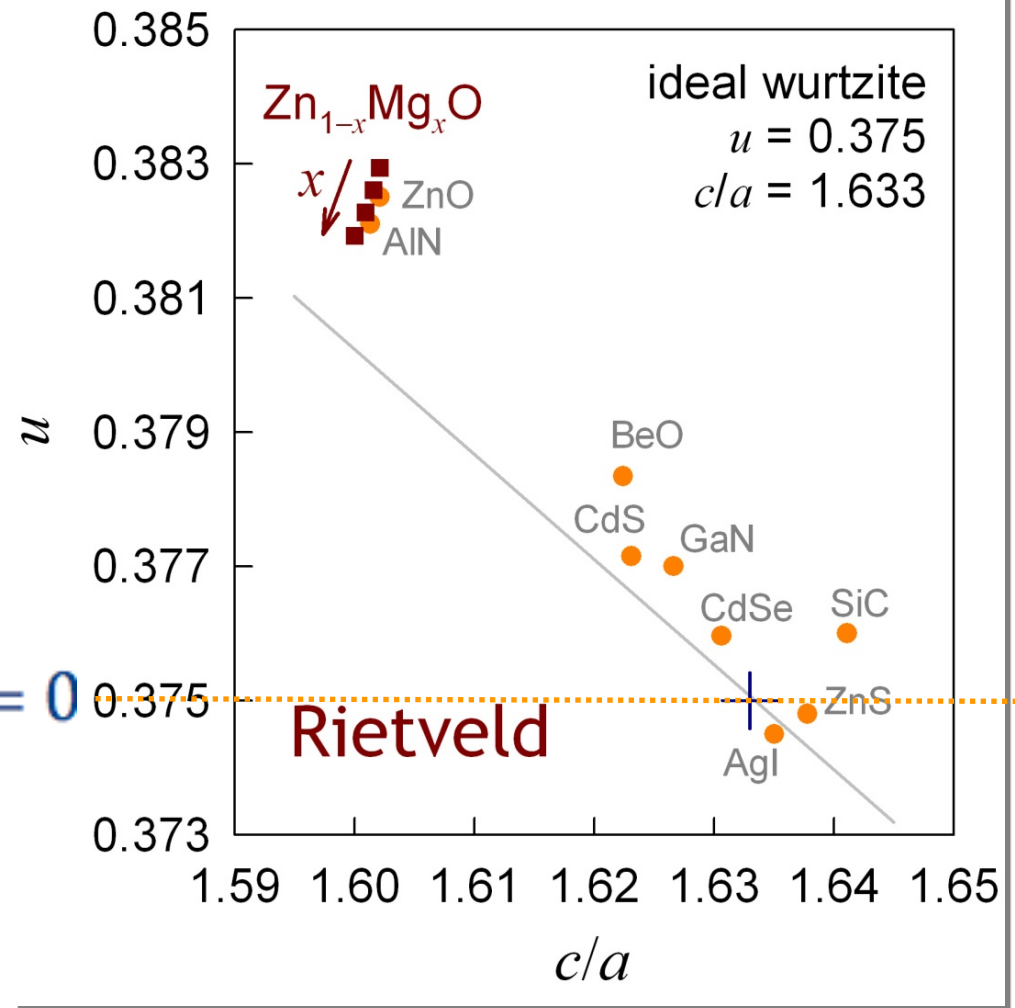
Lonsdaleite

Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors

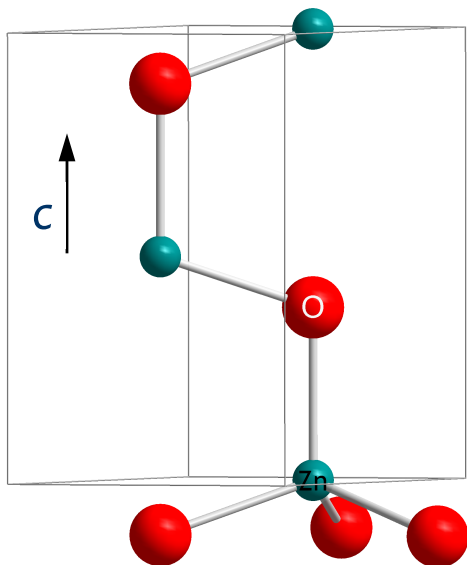
Wurtzite structures and static polarization

[Dr. Young-Il Kim]

$$u = \frac{3}{8}; P_s = 0$$



Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors



Consider one ZnO_4 tetrahedron (polarization unit)

$$\text{Zn} \quad \left(\frac{1}{3}, \frac{2}{3}, 0\right)$$

$$\text{O}_{\text{axial}} \quad \left(\frac{1}{3}, \frac{2}{3}, u\right)$$

$$\text{O}_{\text{basal}} \quad \left(\frac{2}{3}, \frac{1}{3}, u - \frac{1}{2}\right)$$

$$\left(\frac{2}{3}, -\frac{2}{3}, u - \frac{1}{2}\right)$$

$$\left(-\frac{1}{3}, \frac{1}{3}, u - \frac{1}{2}\right)$$

dipole moment along c – direction

$$\mu(\text{Zn}-\text{O}_{\text{axial}}) = \frac{1}{4} \times (-2) \times u \times c$$

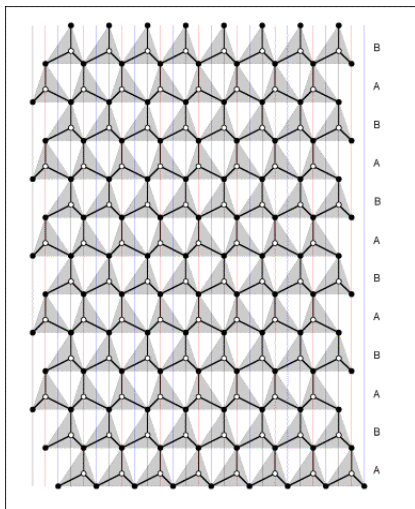
$$\mu(\text{Zn}-\text{O}_{\text{basal}}) = 3 \times \frac{1}{4} \times (-2) \times \left(u - \frac{1}{2}\right) \times c \quad (\text{in } e \cdot \text{\AA})$$

$$P_s = \frac{\mu_{\text{sum}}}{\text{unit volume}} = \frac{-2 \times \left(u - \frac{3}{8}\right) \times c}{\frac{\sqrt{3}}{4} a^2 c} = \frac{-2 \times \left(u - \frac{3}{8}\right)}{\frac{\sqrt{3}}{4} a^2} \left(\frac{e}{\text{\AA}^2}\right) \times \left(1.60 \times 10^3 \frac{\mu\text{C}}{\text{cm}^2} \cdot \frac{\text{\AA}^2}{e}\right)$$

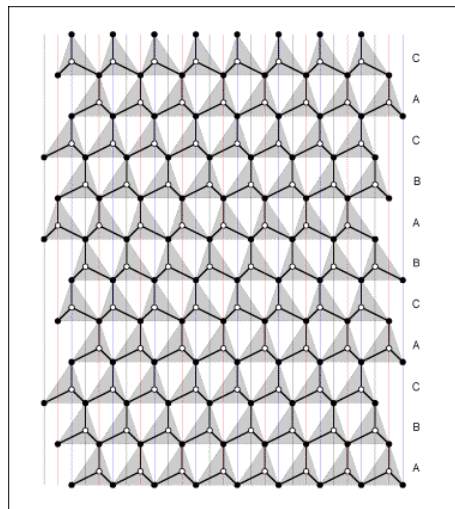
$\left(u - \frac{3}{8}\right) \cdot c$ can be obtained also from the separation between centers of (-) and (+) charges.

[Dr. Young-Il Kim]

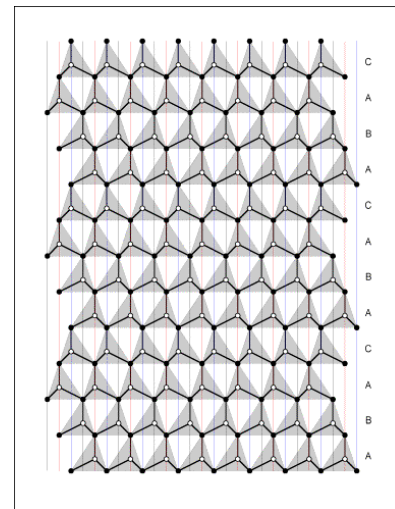
Polytypism in SiC



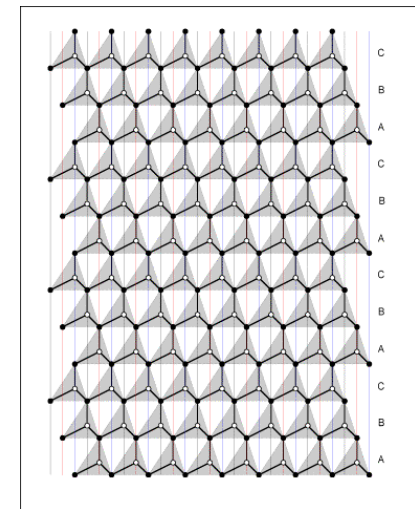
3C



4H



3H



2H

Specifying the total number of layers in the hexagonal unit cell followed by the letter *H*, *R* or *C* to indicate the lattice type. Thus a symbol *nH* represents a structure with *n* layers in the primitive hexagonal unit cell while *mR* denotes a structure whose primitive lattice is rhombohedral and contains *m* layers in its hexagonal unit cell.

Ramsdell notation.

Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors

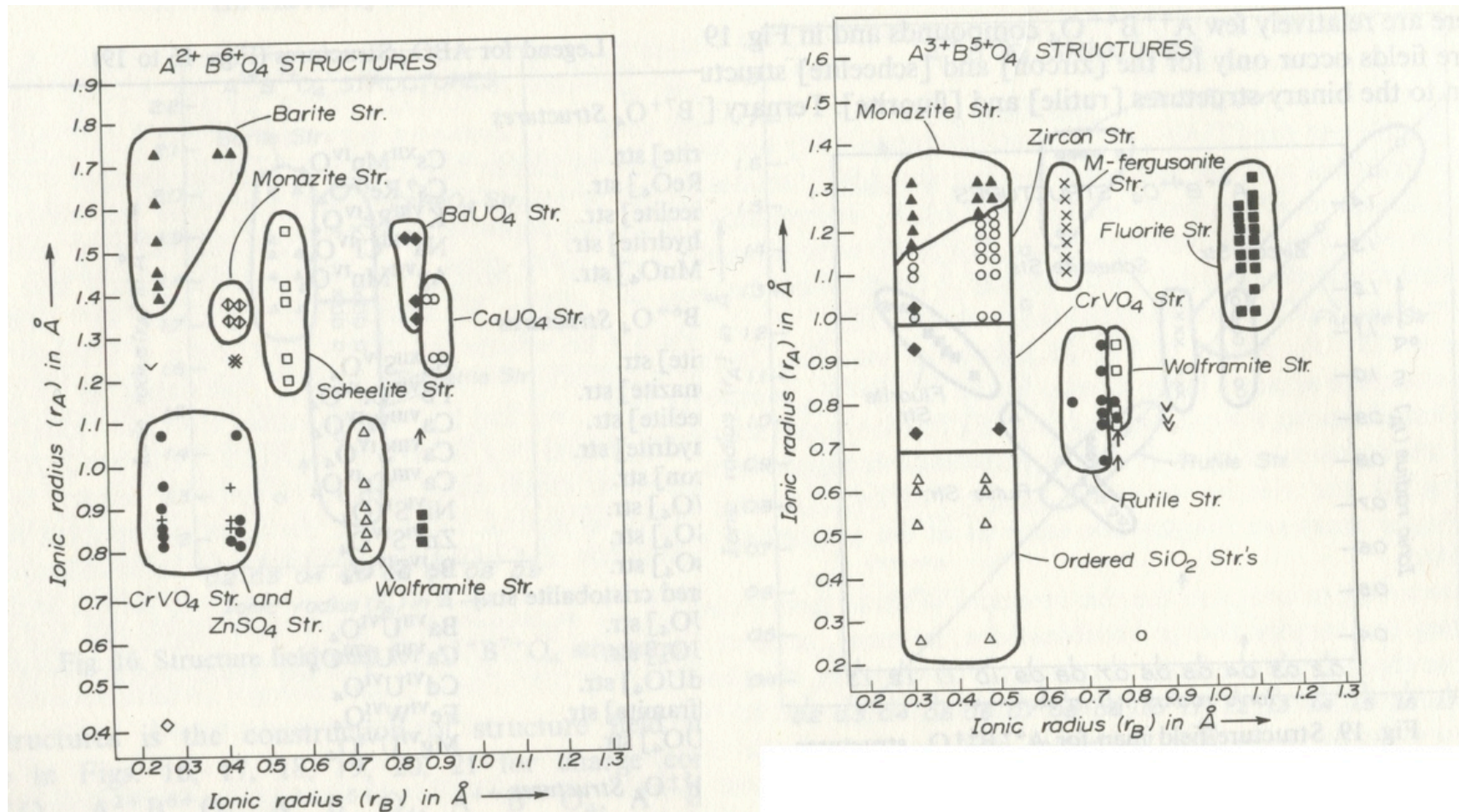
Stacking notation

Ramsdell notation	ABC sequence	Zhdanov number	h-c notation
2H	AB	(11)	h
3C	ABC		c
4H	ABCB	(22)	hc
6H ₁	ABCACB	(33)	hcc
6H ₂	ABCBAB	(2211)	hchchh
9R	ABACACBCB	(12)	hhc

<http://www.iucr.org/iucr-top/comm/cteach/pamphlets/5/node0.html>

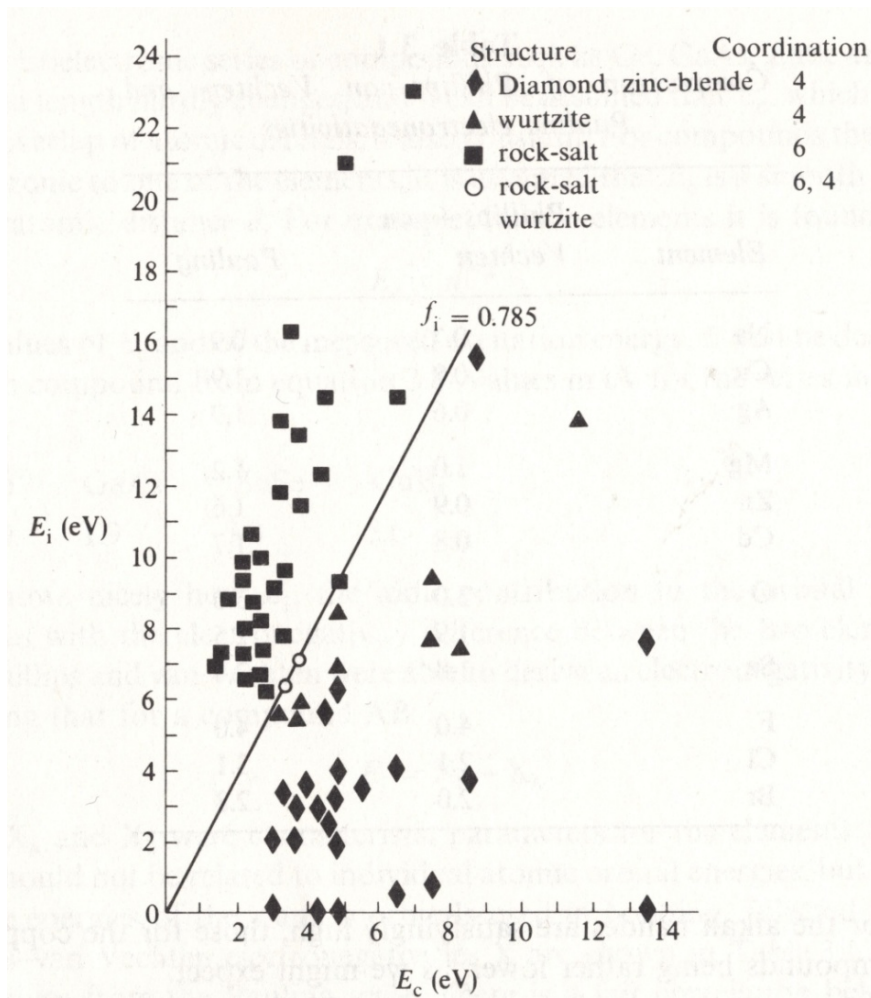
Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors

Structure sorting: The major ternary structural families, Muller and Roy.



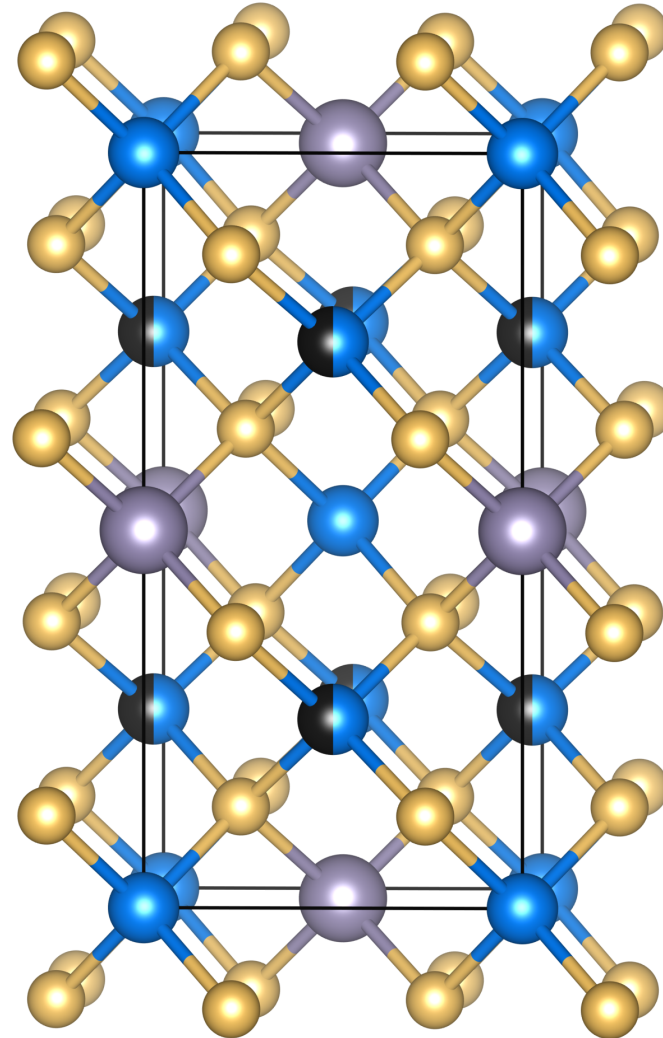
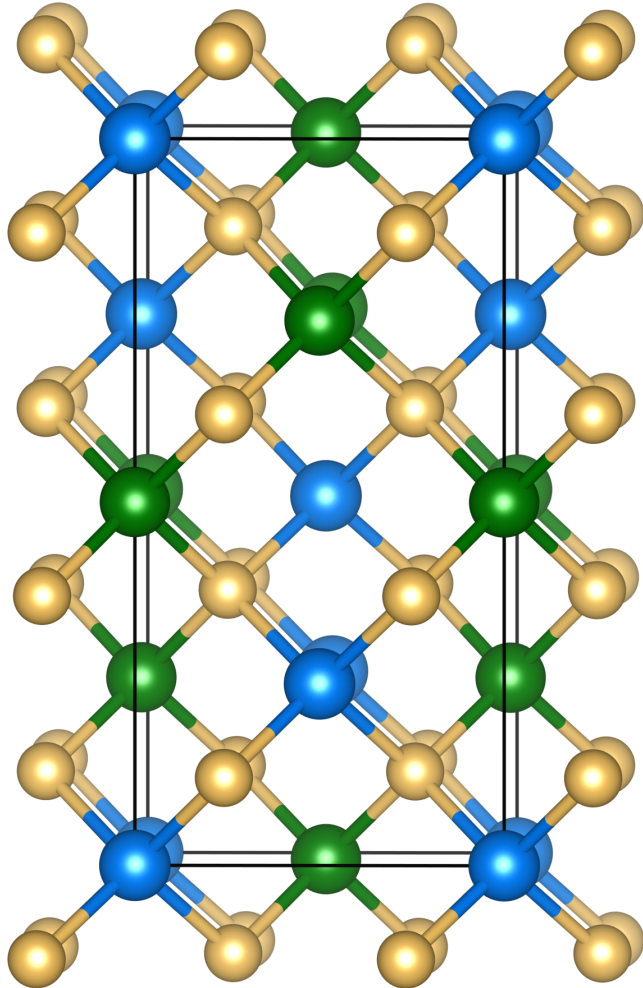
Class 2: fcc, hcp, diamond, zinc blende, wurtzite, SiC, semiconductors

Semiconductors: Structure sorting (Phillips-van Vechten)



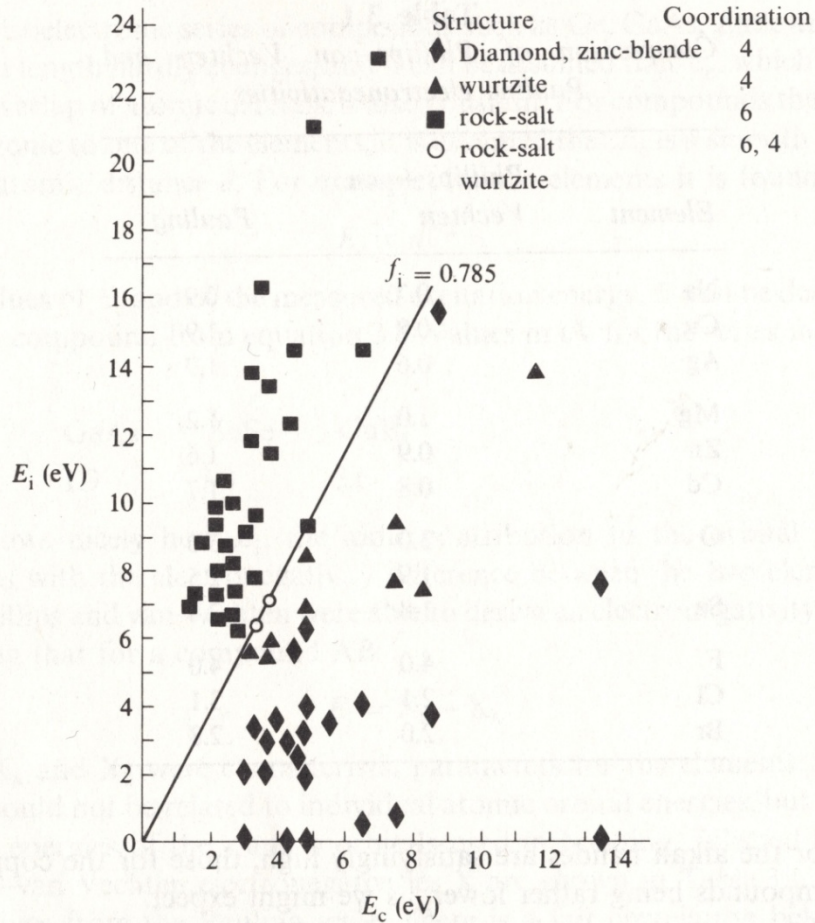
Class 2: *fcc*, *hcp*, diamond, zinc blende, wurtzite, SiC, semiconductors

Chalcopyrite: CuFeS_2 and Kesterite, $\text{Cu}_2\text{ZnSnS}_4$

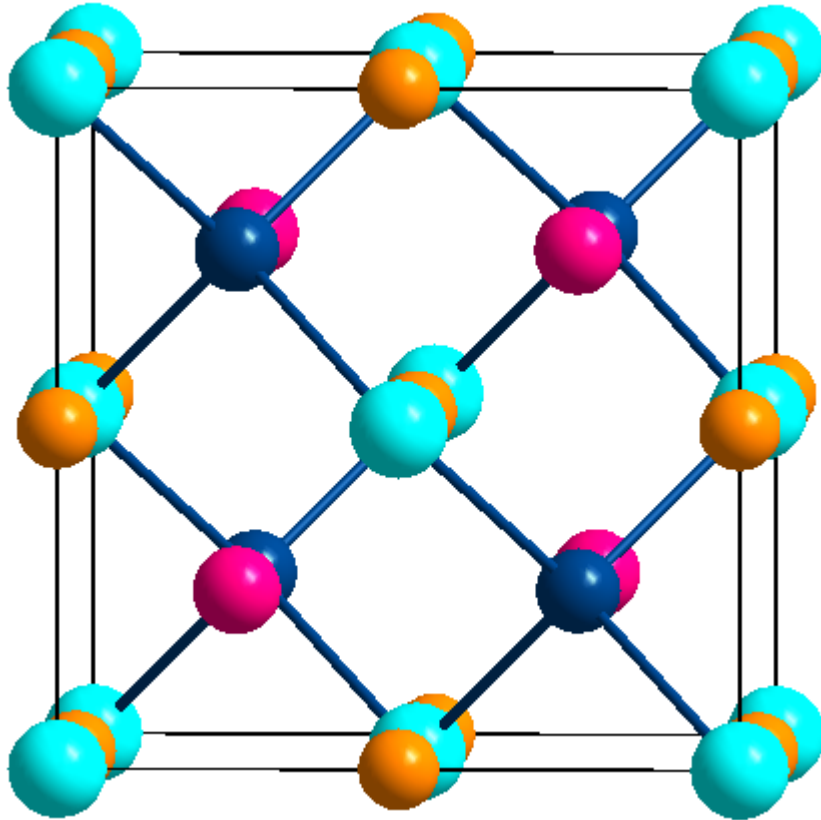


Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

Semiconductors: Structure sorting (Phillips-van Vechten)

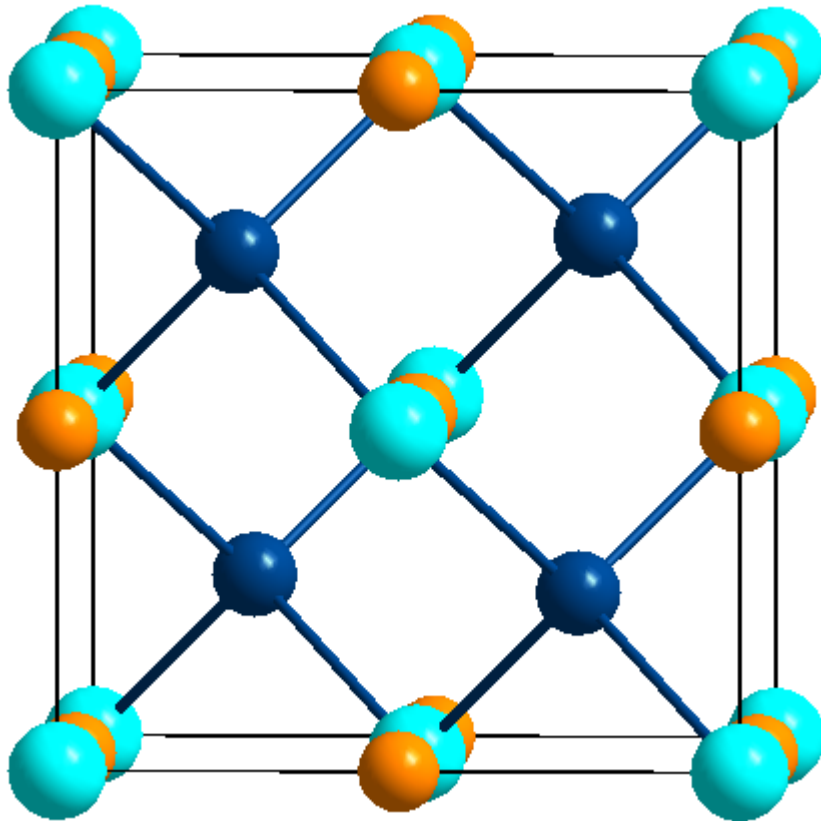


Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



The Heusler crystal structure: XY_2Z
F. Heusler (1903)
4 interpenetrating fcc lattices.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

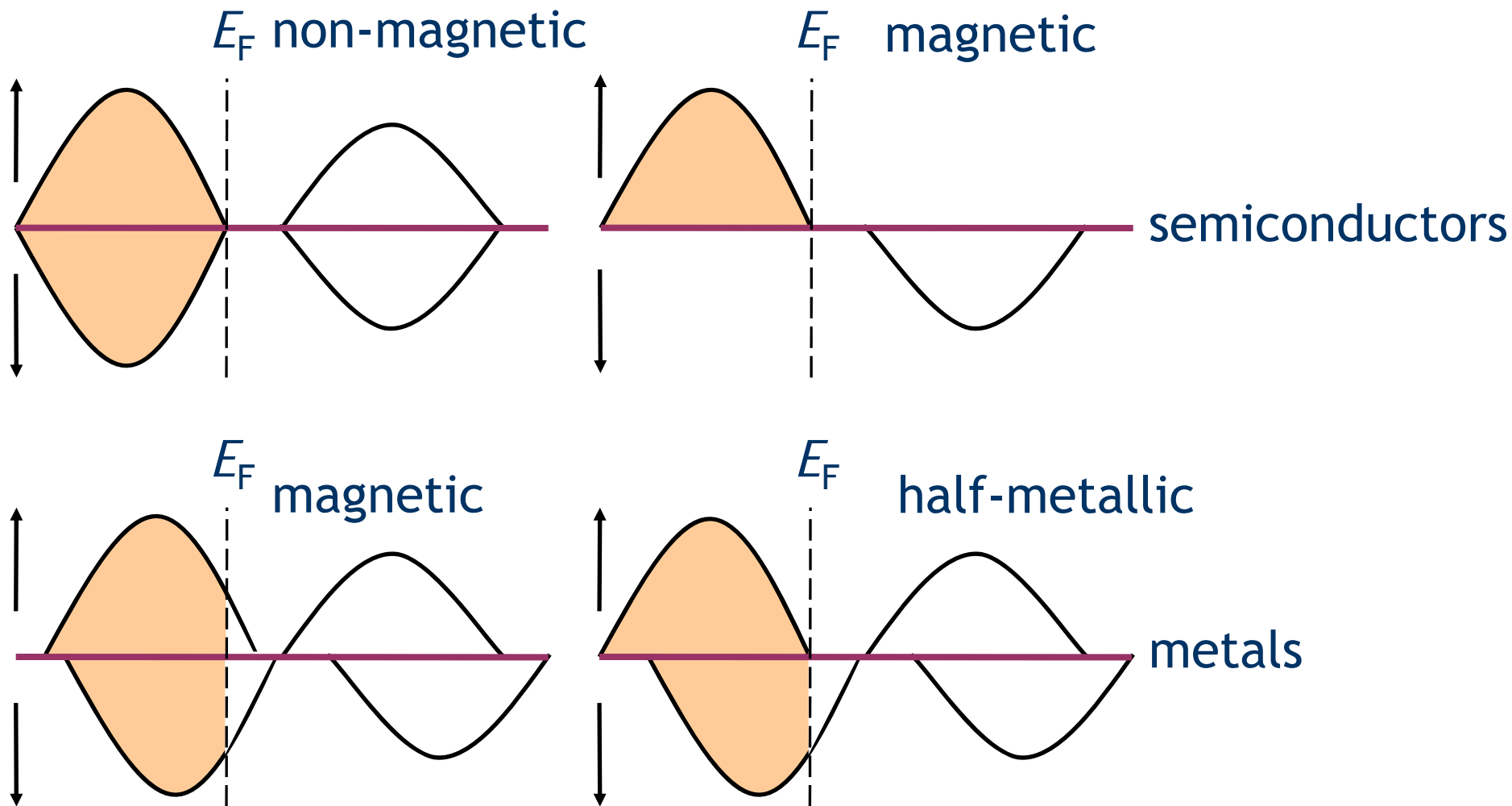


The half-Heusler crystal structure: XYZ. 3 interpenetrating fcc lattices.

AXZ rock-salt with Y in one of the tetrahedral voids.

YZ zinc-blende with X in an octahedral void.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



New Class of Materials: Half-Metallic Ferromagnets

R. A. de Groot and F. M. Mueller

Research Institute for Materials, Faculty of Science, Toernooiweld, 6525 ED Nijmegen, The Netherlands

and

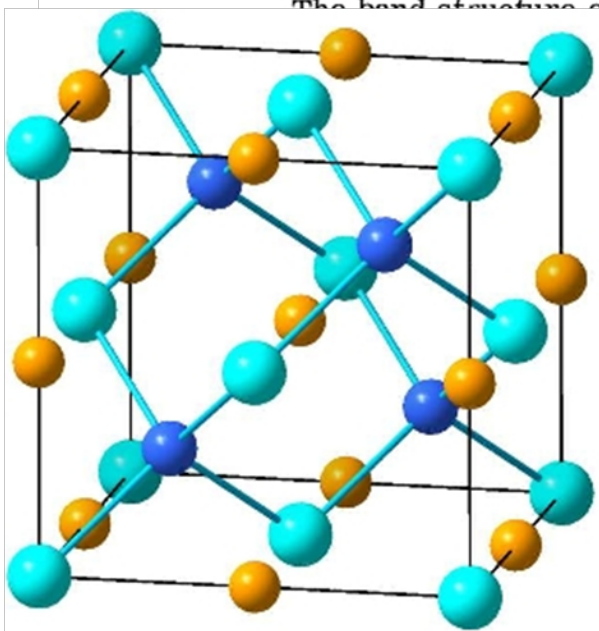
P. G. van Engen and K. H. J. Buschow

Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

(Received 21 March 1983)

The band structure of Mn-based Heusler alloys of the $C1_b$ crystal structure (MgAgAs) is calculated with the augmented-spherical-wave method. Some of these alloys show unusual electronic properties. The majority-spin electrons are metallic, while the minority-spin electrons are semiconducting.

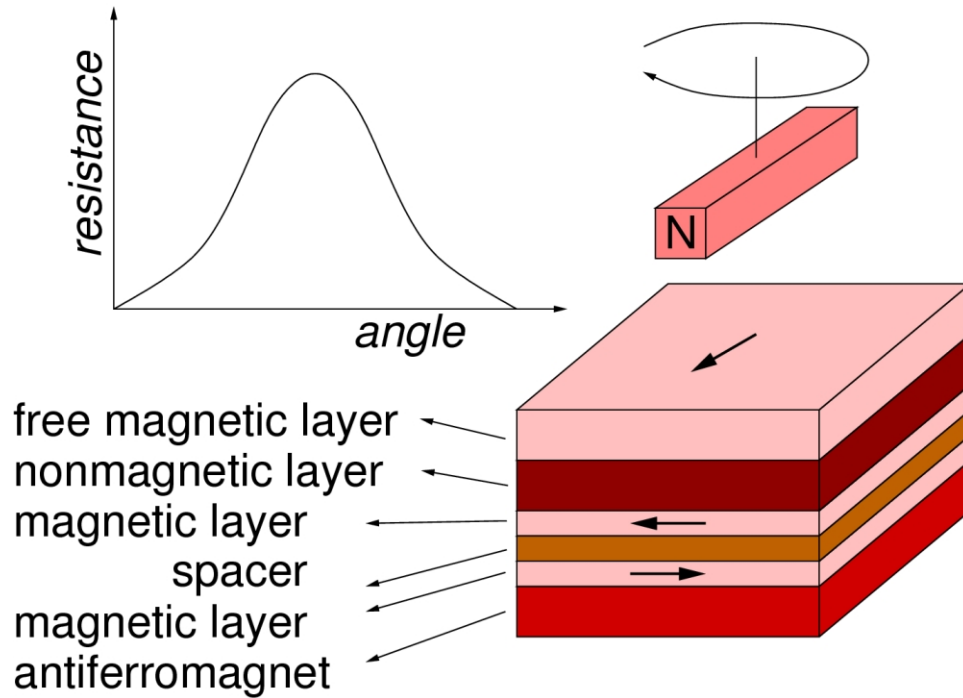
PHYS. REV. LETT. 51, 1551 (1983)
DOI: 10.1103/PhysRevLett.51.1551



Half Heusler MnNiSb

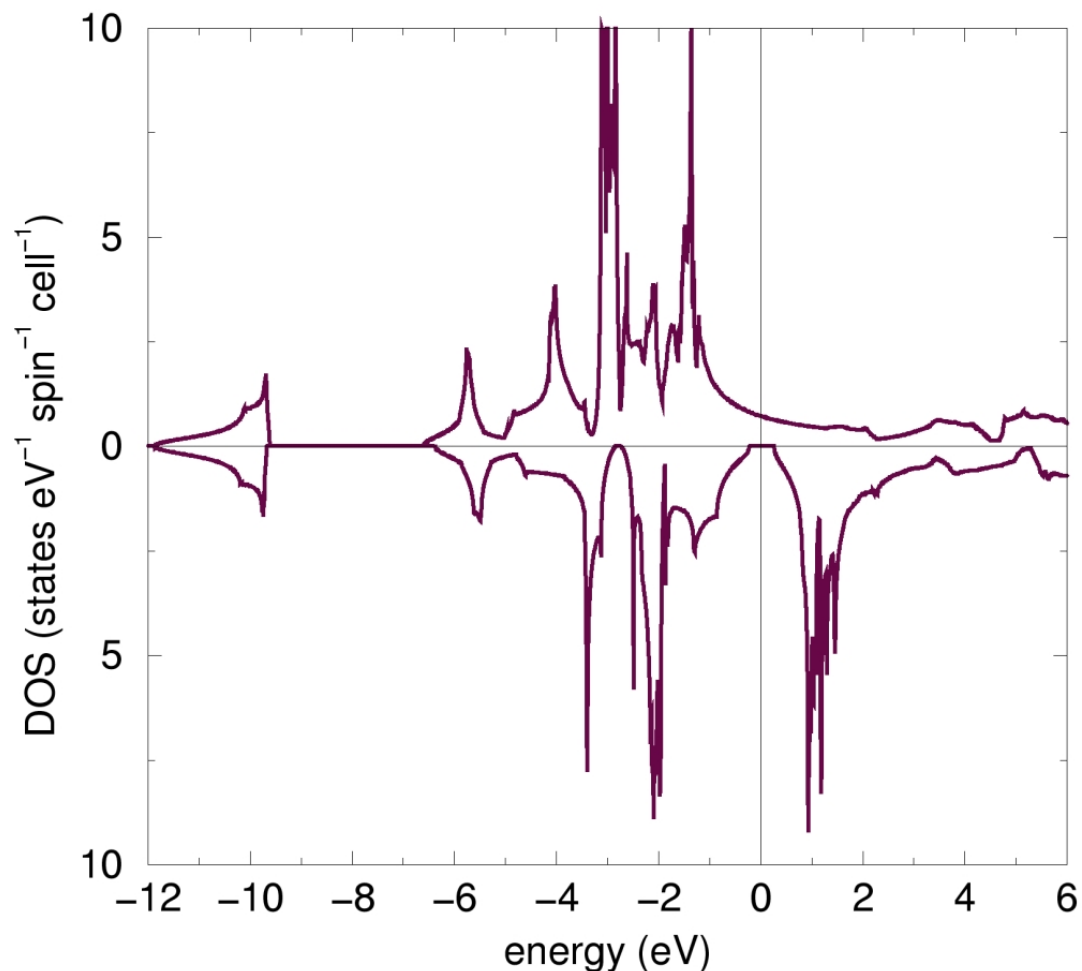
Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

Magnetoresistive angle sensor:



Modified from Grünberg,
Phys. Today 54 (2001) 34

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



MnNiSb (deGroot 1983) has states at the Fermi energy only in one spin direction, and is gapped in the other. The calculated magnetic moment is precisely $4 \mu_B$

Molecular-beam epitaxy of the half-Heusler alloy NiMnSb on (In,Ga)As/InP (001)

P. Bach,^{a)} A. S. Bader, C. Rüster, C. Gould, C. R. Becker, G. Schmidt, and L. W. Molenkamp

Physikalisches Institut (EP3), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

W. Weigand, C. Kumpf, and E. Umbach

Physikalisches Institut (EP2), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

R. Urban, G. Woltersdorf, and B. Heinrich

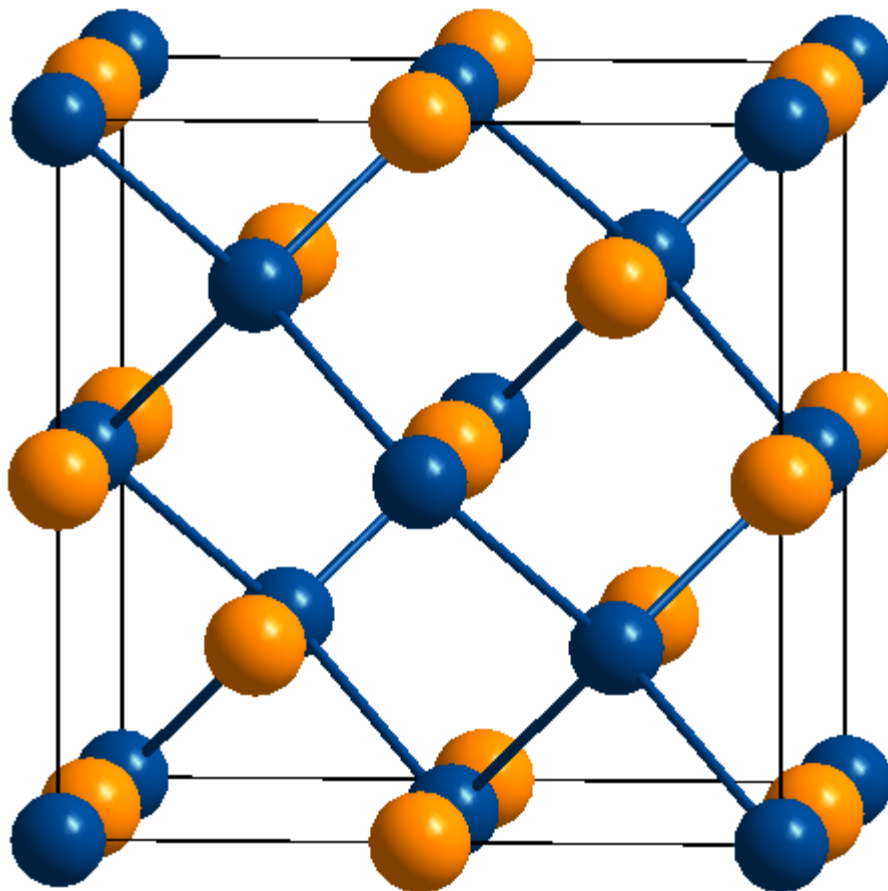
Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada

(Received 17 March 2003; accepted 4 June 2003)

We report the growth of the half-Heusler alloy NiMnSb on InP (001) by molecular-beam epitaxy using a lattice-matched (In,Ga)As buffer. High-resolution x-ray diffraction confirms a high crystalline quality. Spot-profile analysis low-energy electron diffraction measurements show well-defined surface reconstructions. The samples show the expected high Curie temperature and an uniaxial anisotropy. © 2003 American Institute of Physics. [DOI: 10.1063/1.1594286]

Half-Heuslers are nearly epitaxial with GaAs: The possibility of spin injection into semiconductors. This is important for any spin-based electronics.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



The Zintl-Klemm concept and valence compounds: The example of LiAl (Li^+Al^-). Al^- is isoelectronic with C and forms a diamond lattice. The Li^+ ions stuff the Al^- lattice. Note the 8 electron rule operates.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

The contribution of Whangbo *et al.* (2000), also Ögüt and Rabe (1995), Galanakis *et al.* (2002):

Instead of 8 electrons, 18 valence electrons suggests a gap. For example, TiNiSn and TiCoSb are 18 electron semiconductors.

TiCoSb = Ti⁴⁺ + (CoSb)⁴⁻; (CoSb)⁴⁻ = GaSb forming a zinc-blende lattice. Ti is in the octahedral hole.



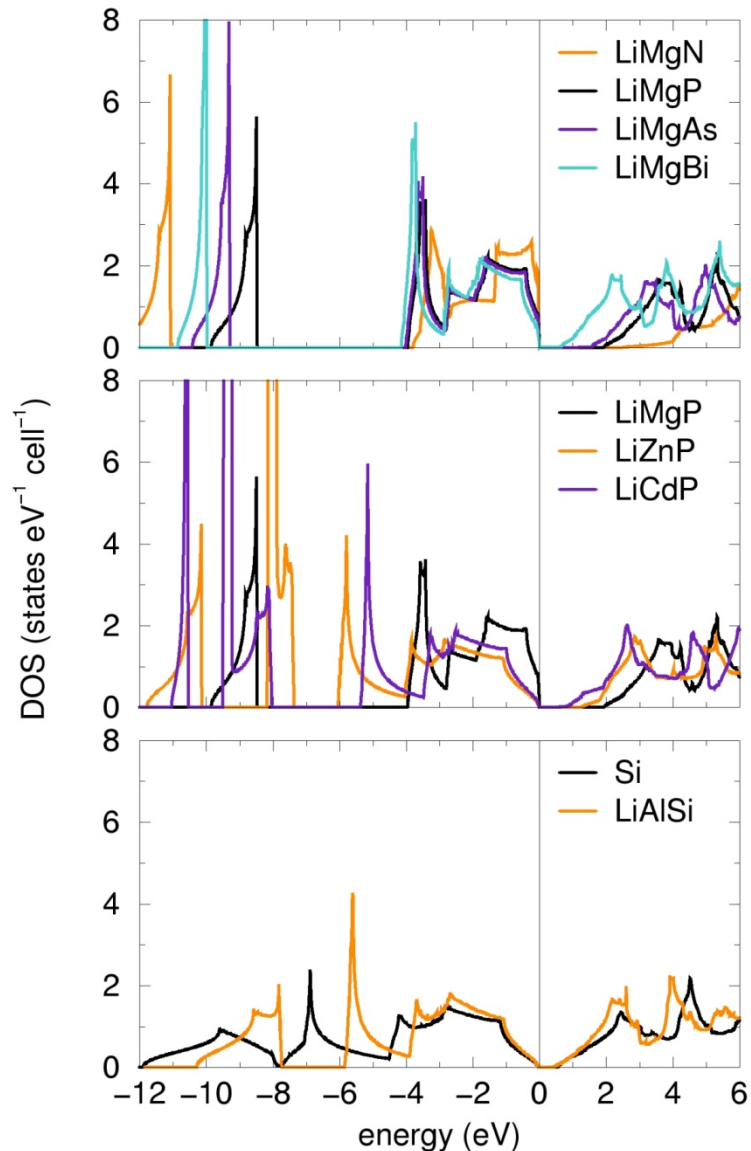
Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

Magnetic compounds (Whangbo): If the number of electrons is 17 or 19, a paramagnet or a Stoner ferromagnet results depending on the DOS at the Fermi energy. If it is 22 (MnNiSb), a local-moment ferromagnet is formed.

What are the precise nature of the gaps ? How do different constituent elements affect the gaps ? How good is the covalent description of the zinc-blende lattice ?

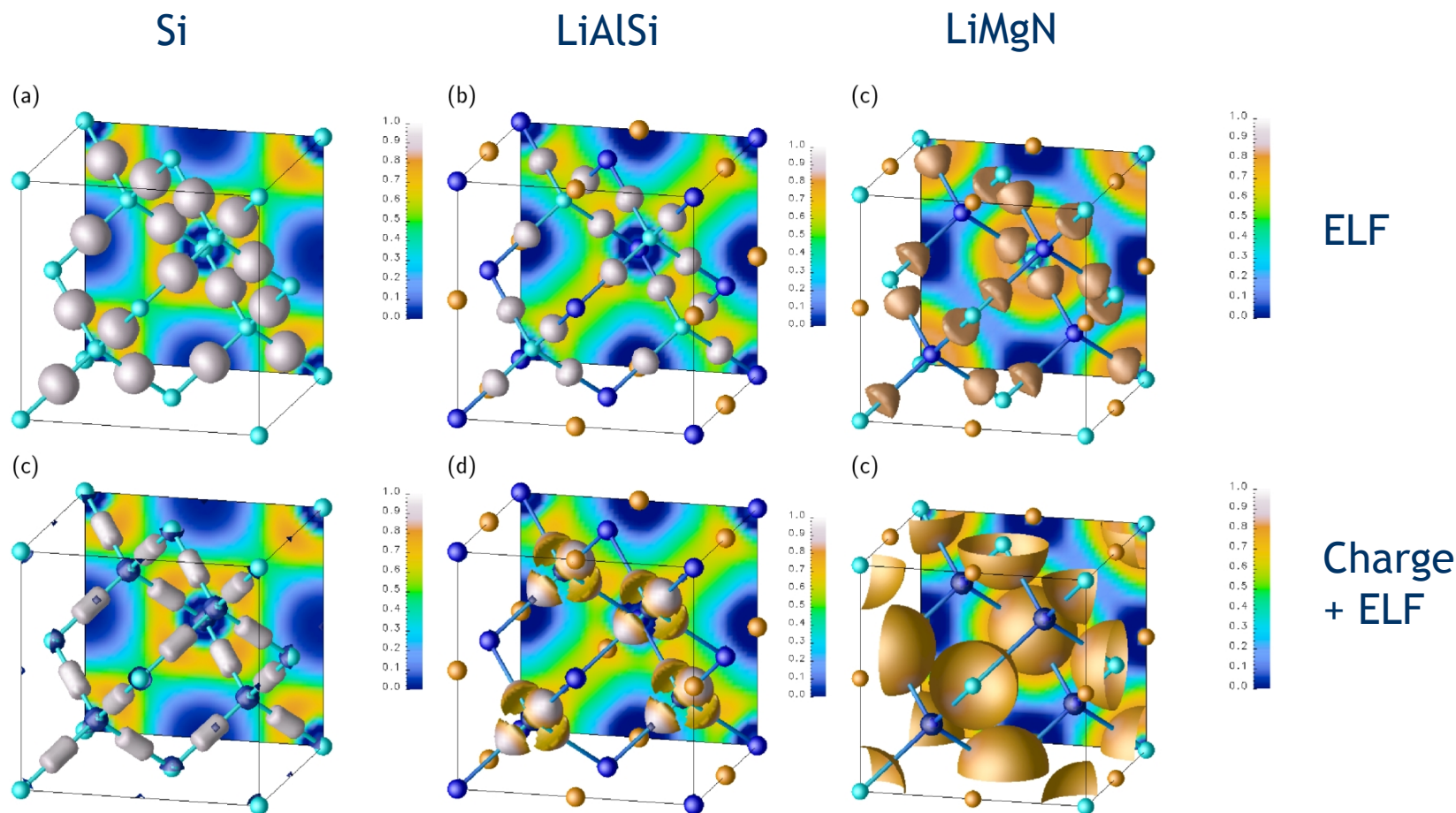
Gaps in semiconductors as well as in the half-metals.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



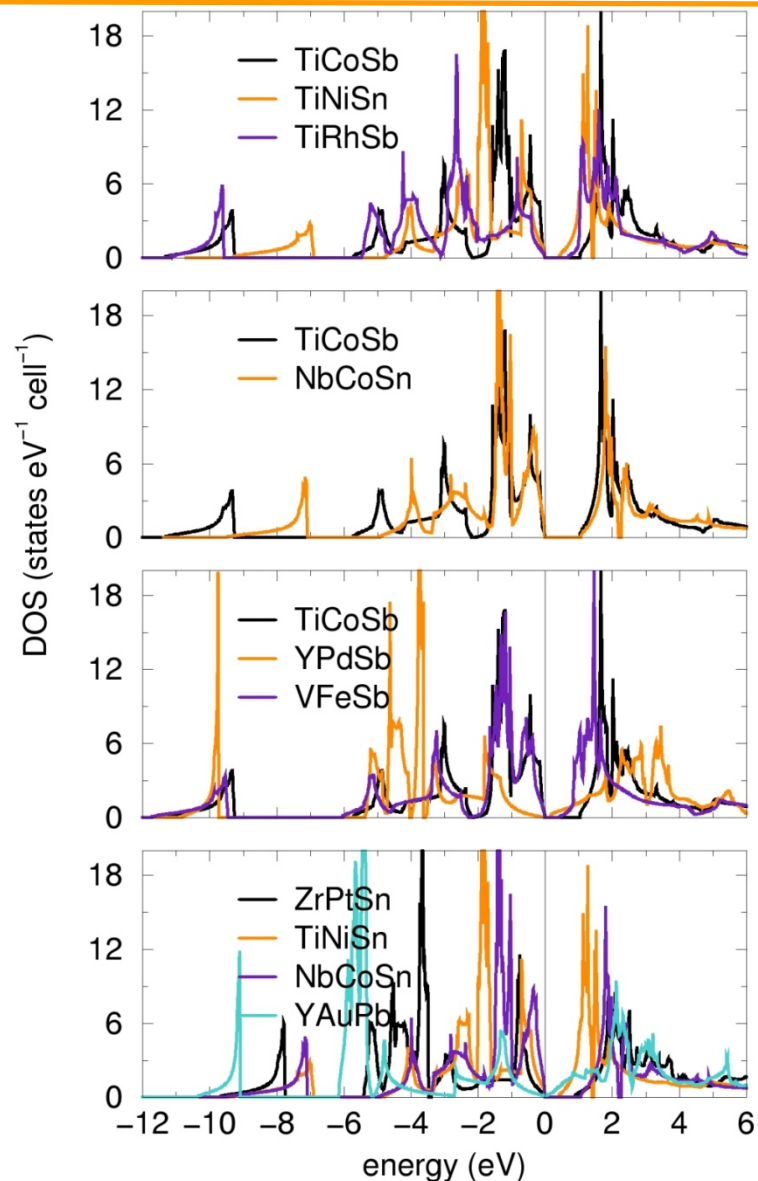
LMTO DOS of 8e half-Heuslers indicates a strong dependence of the band gap on composition of the zinc-blende lattice.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



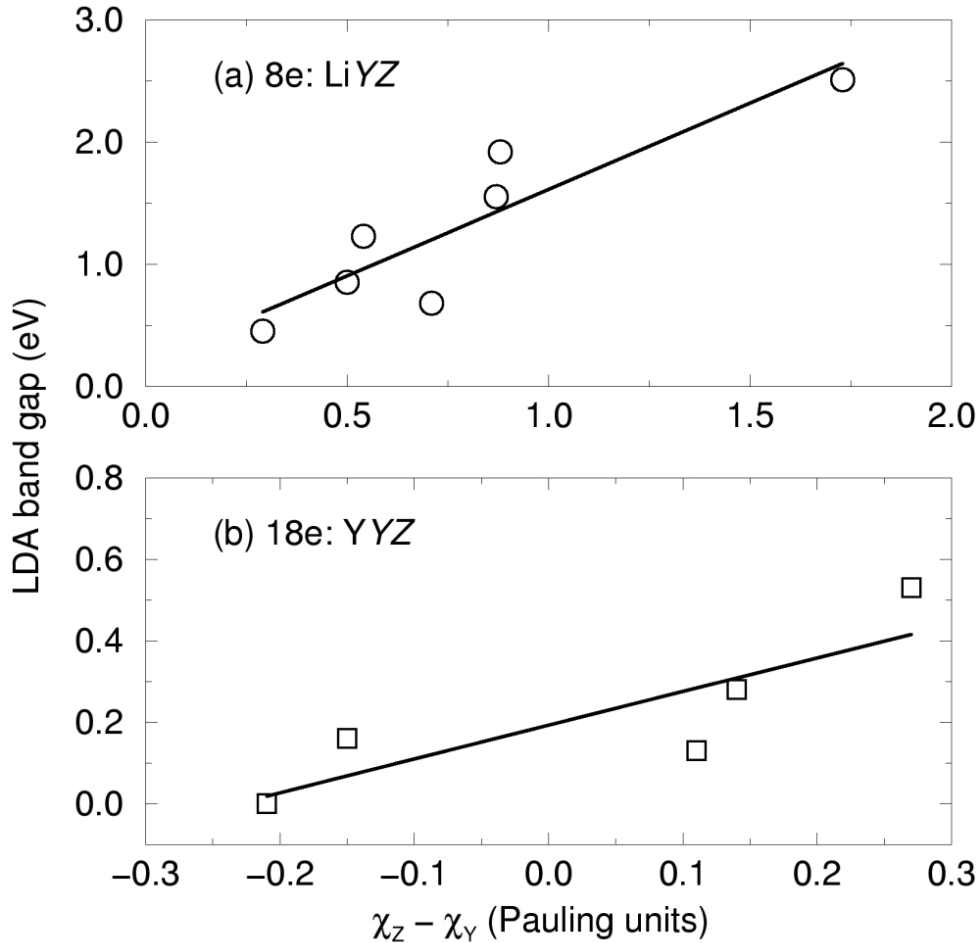
Electron localization functions of the δe compounds show strongly localized bonding.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



LMTO DOS of 18e half-Heuslers also show rather simple trends in their band gaps.

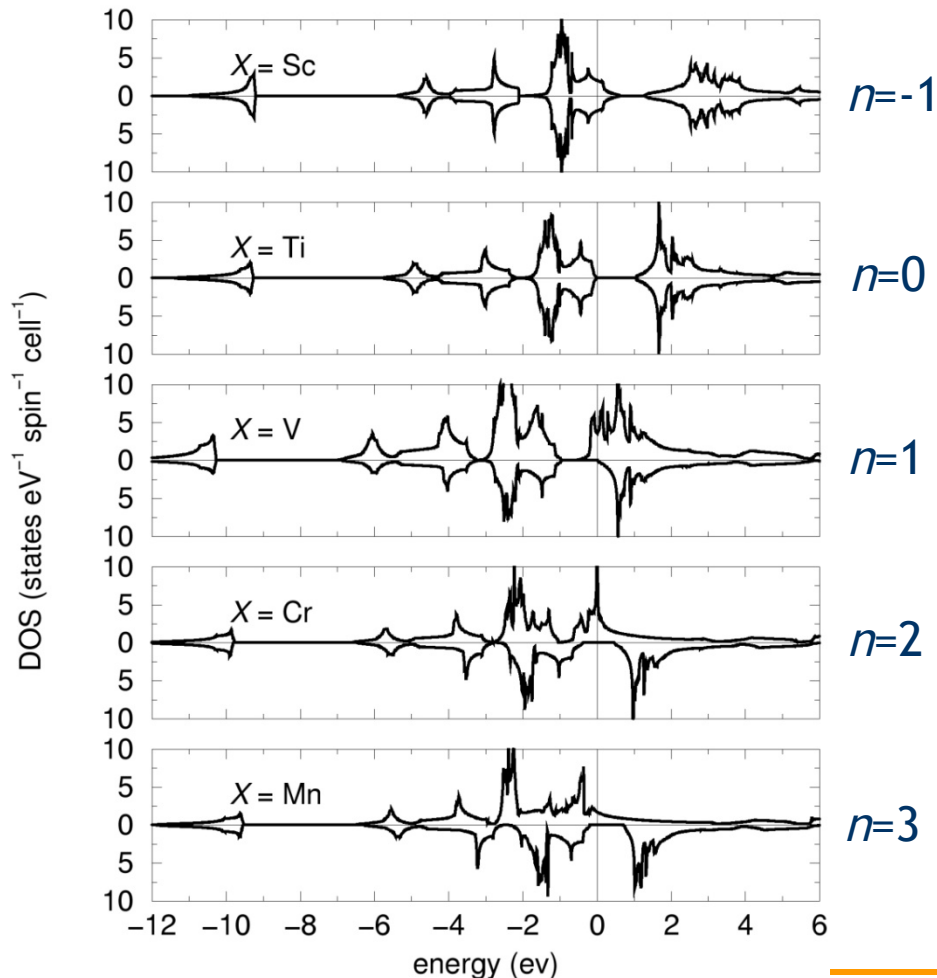
Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers



The band gaps of some 8e and 18e half-Heuslers depend on the electronegativity of the ions in the zinc-blende framework.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

$X\text{CoSb}$

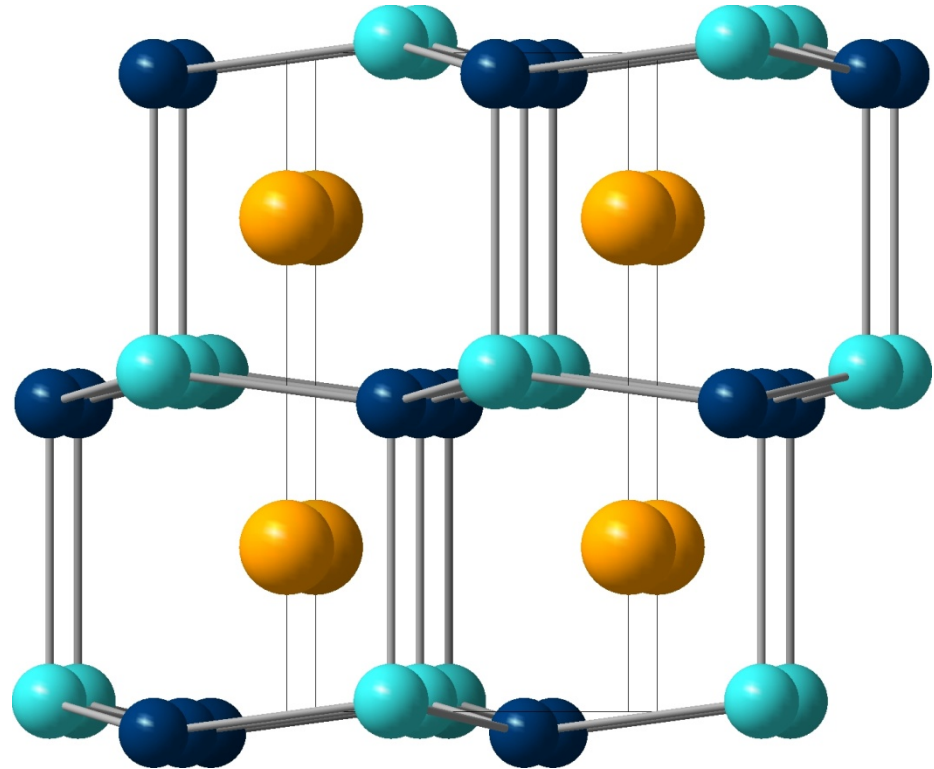


Magnetic half-Heusler compounds can also be thought of as stuffed zinc-blendes. The band/half-metallic gaps are a little more complex.

Class 3: Semiconductors, stuffed zinc blende, half and full Heuslers

Can one equivalently look for stuffed wurtzites: *hexagonal* semiconducting and half-metallic analogues of the half-Heuslers? The structure type is known: LiGaGe (SG. $P6_3mc$). Many possibly incorrect determinations in CaIn_2 structure.

The structure shown here is CePdSb. Best described as Ce^{3+} stuffing a $(\text{PdSb})^{3-}$ wurtzite lattice, although the $(\text{PdSb})^{3-}$ network is nearly flat/graphitic.



3D topological insulators and half-Heusler compounds

Ram Seshadri

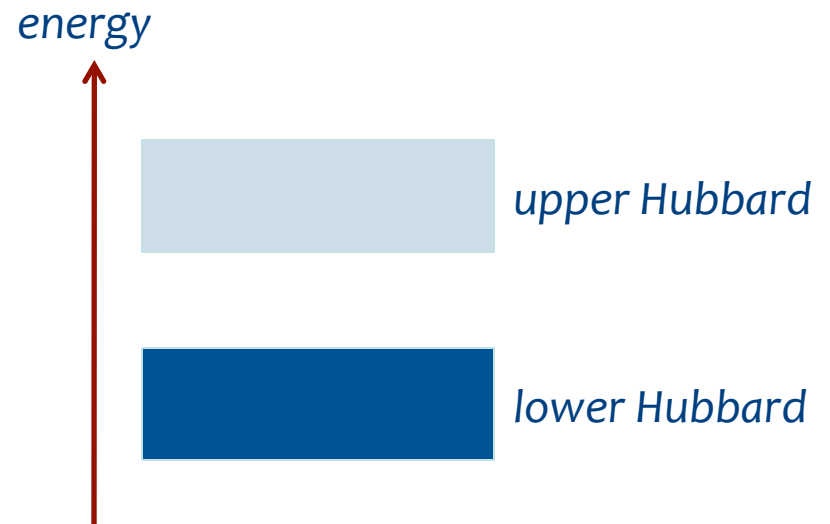
*Materials Department, and
Department of Chemistry and Biochemistry
Materials Research Laboratory
University of California, Santa Barbara CA 93106
<http://www.mrl.ucsb.edu/~seshadri> +++ seshadri@mrl.ucsb.edu*

Trivial (normal) insulators:

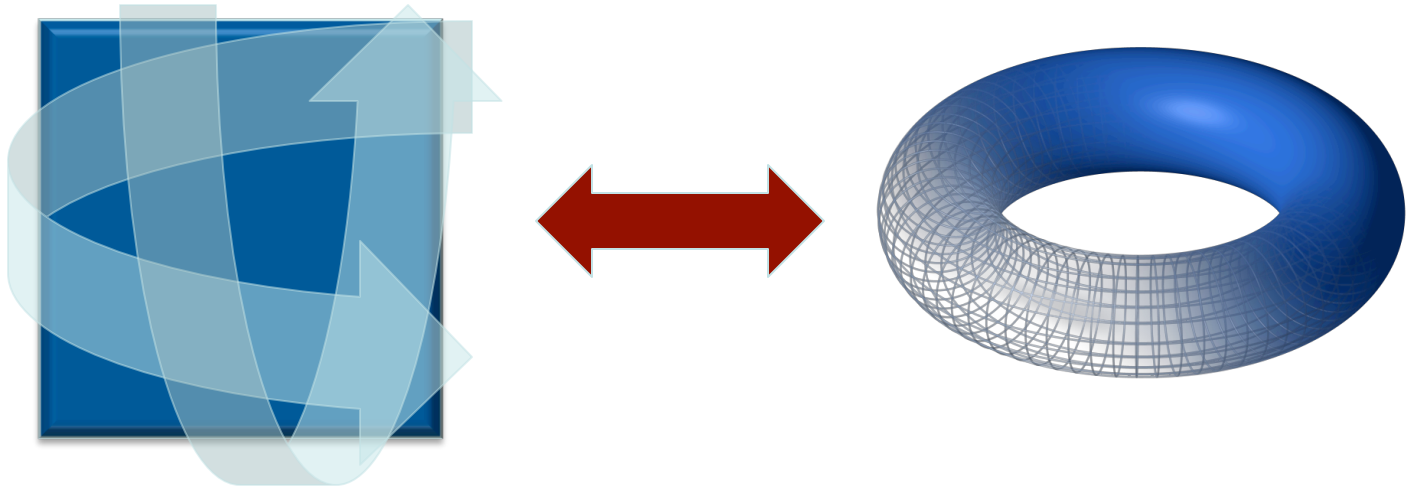
Band insulators: (eg. Si)



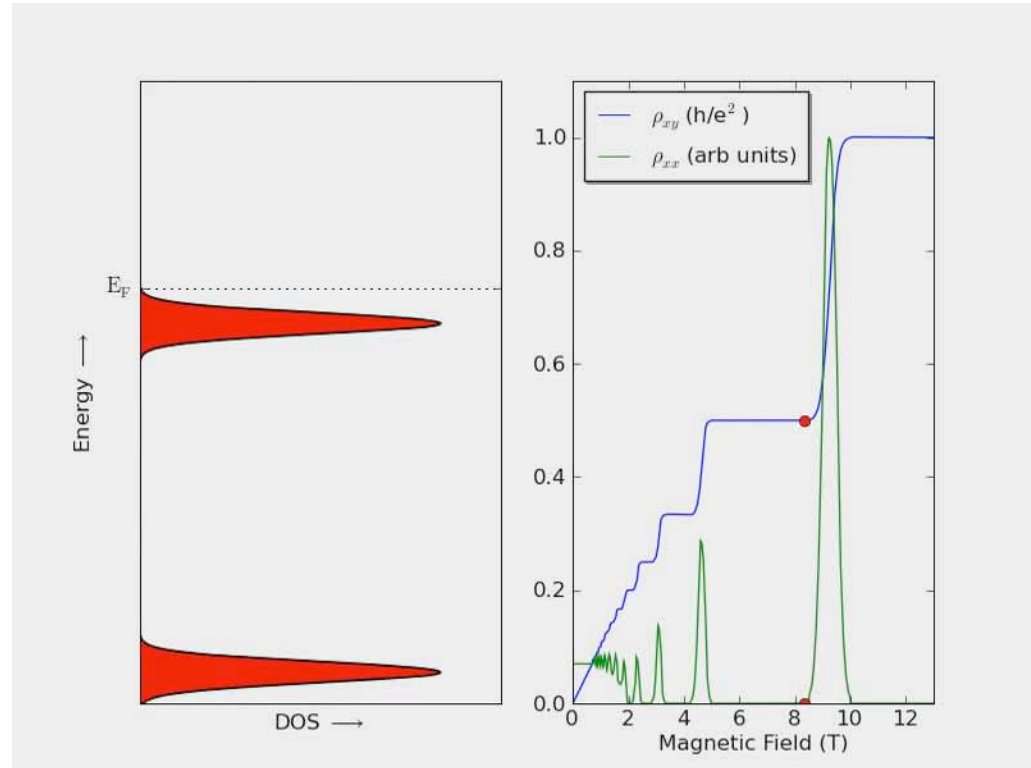
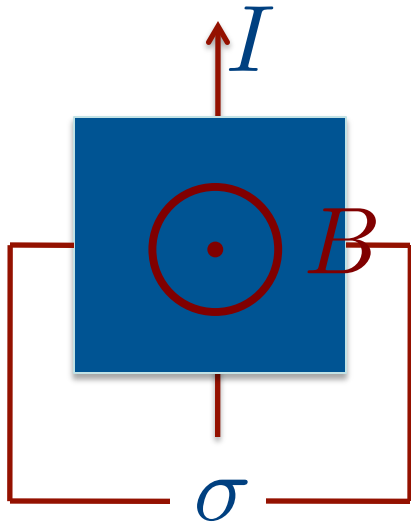
Mott-Hubbard insulators: (eg. MnO)



two-dimensional systems correspond to tori etc.



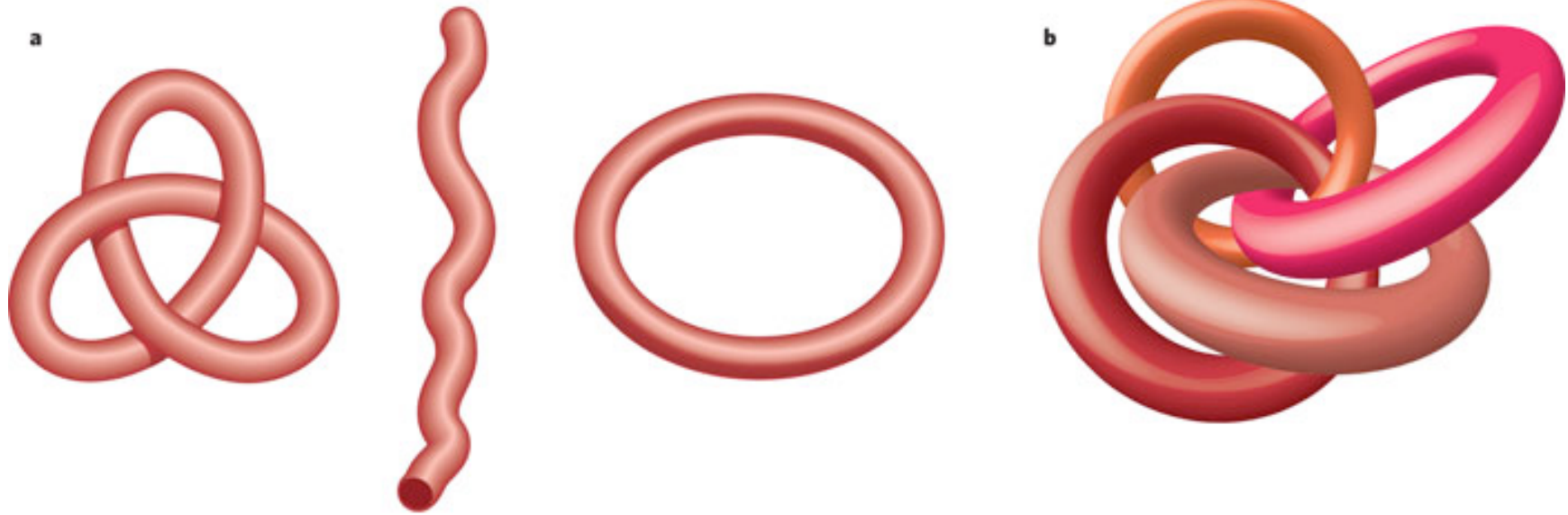
The quantum Hall effect:



Landau levels of electrons in 2D orbiting an external magnetic field become highly degenerate at high fields. For sufficiently strong B -fields, each Landau level may have so many states that all of the free electrons in the system sit in only a few Landau levels and the quantum Hall effect is observed:

$$\sigma = \nu \frac{e^2}{h}$$

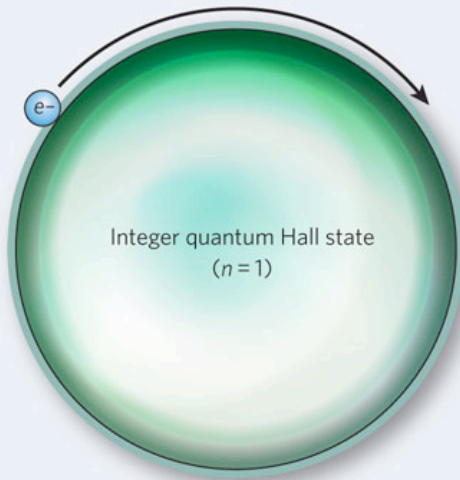
Instead of being driven by such an external magnetic field, electrons could, in principle, form a quantum Hall state driven by forces that result from spin-orbit coupling, a relativistic effect in which the spin and orbital angular momentum degrees of freedom of electrons are coupled; this coupling causes electrons that are moving through a crystal to feel a *spin-dependent* force, even in non-magnetic materials.



(a) An illustration of topological change and the resultant surface state. The trefoil knot (left) and the simple loop (right) represent different insulating materials: the knot is a topological insulator, and the loop is an ordinary insulator. Because there is no continuous deformation by which one can be converted into the other, there must be a surface where the string is cut, shown as a string with open ends (centre), to pass between the two knots; more formally, the topological invariants cannot remain defined. *If the topological invariants are always defined for an insulator, then the surface must be metallic.*

(b) The knotting in real topological insulators is more complex as these require a minimum of four electronic bands, but the surface structure that appears is relatively simple

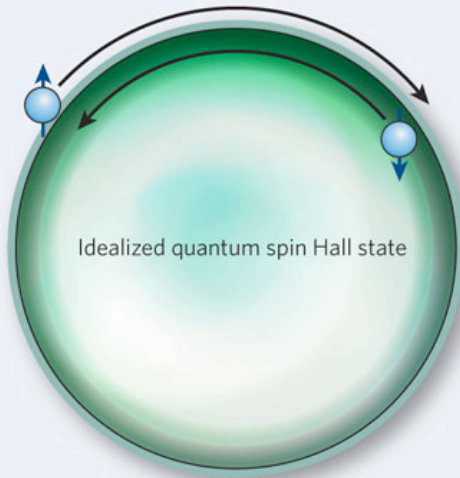
a



Ordinary insulator

(a) Edge of an integer quantum Hall state. The electrons (e^-) are confined to a 2D insulating droplet with a metallic edge. Along the edge, electrons propagate only in one direction, which is determined by the sign of the applied magnetic field perpendicular to the droplet.

b

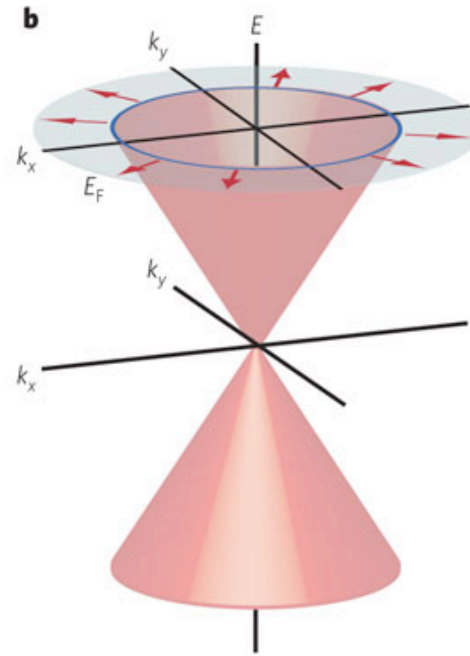
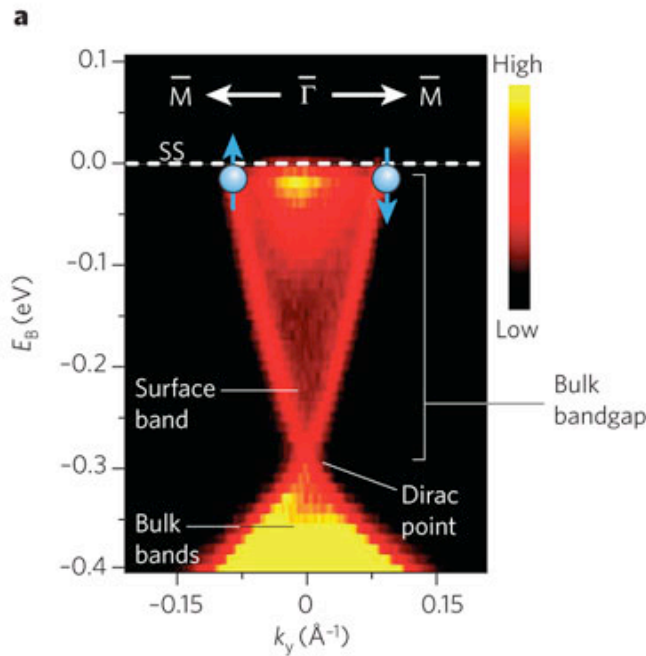


Ordinary insulator

(b) Edge of an idealized quantum spin Hall state (that is, a 2D topological insulator). Along the edge, spin-up electrons move clockwise, whereas spin-down electrons move anticlockwise. Spin-up and spin-down electrons are independent and are in oppositely directed quantum Hall states.



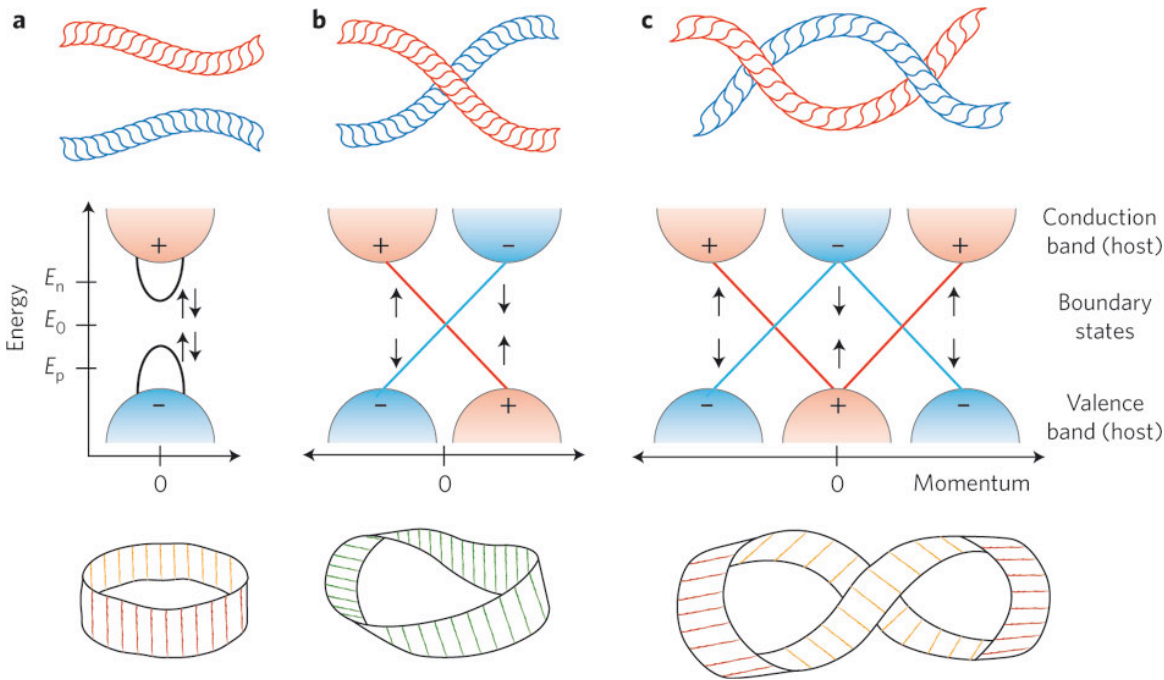
The birth of topological insulators [Moore, *Nature* 464 (2010) 194-197]



(a) The electronic structure of Bi_2Se_3 , as measured by ARPES. Measured energy electron energy, E_B , is plotted against electron momentum, k_y . High intensity (red and yellow areas) indicates a non-zero electronic density of states. The surface bands crossing the bulk bandgap enclose a single Dirac point at the Brillouin-zone centre (Γ), which is the signature that this material is a topological insulator. indicates the centre of an edge of the Brillouin zone, and the path in the Brillouin zone is indicated by white arrows. The direction of electron spin is indicated by blue arrows.

(b) Theoretical idealization of the electronic structure of Bi_2Se_3 , showing the rotation of the spin degree of freedom (red arrows) as an electron (with energy E) moves around the Fermi surface (with Fermi energy E_F).

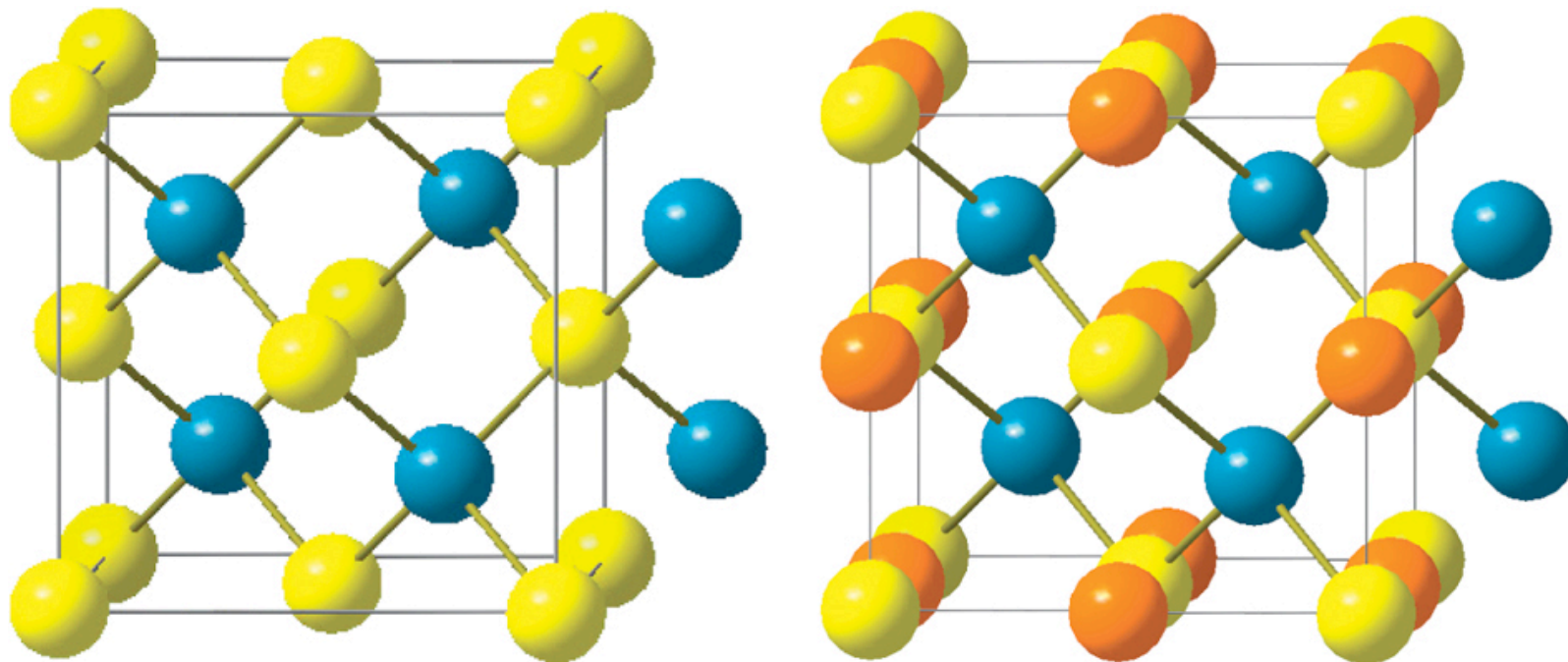
Topological insulators, A romance with many dimensions [Manoharan, *Nature Nanotechnol.* 5 (2010) 477-479]



(a) The conduction and valence bands of a typical 3D solid (middle section). The shaded regions are the bands in the bulk of the solid, and the thick black lines are the bands at the surface. In general, the conduction band is symmetric (red), the valence band is antisymmetric (blue), and spin-up and spin-down electrons (black arrows) have the same energy. (b) Spin-orbit coupling lifts the degeneracy of the electron spins and leads to other changes: in the bulk, for example, the conduction band becomes antisymmetric (-) and the valence band becomes symmetric (+). At the boundary the bands (the red and blue lines) actually cross over each other, and the Fermi energy is forced to intersect both bands, which results in the conduction of electric charge along the boundary.

Tunable multifunctional topological insulators in ternary Heusler compounds

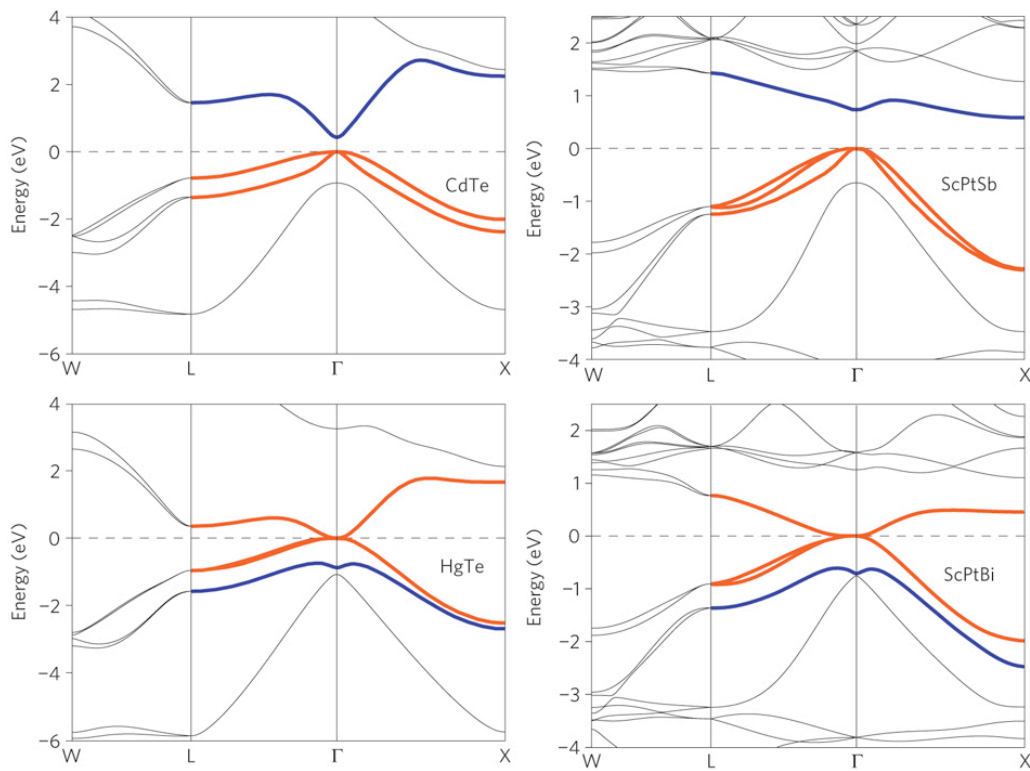
Chadov *et al. Nature Mater.* 9 (2010) 541-545



The zinc-blende (XY) structure is shown on the left, and the C1b (XYZ) on the right. Yellow and blue spheres correspond to the main-group (Z) and transition (Y) elements, respectively. The orange spheres in C1b stand for the additional stuffing (X) element.

Tunable multifunctional topological insulators in ternary Heusler compounds

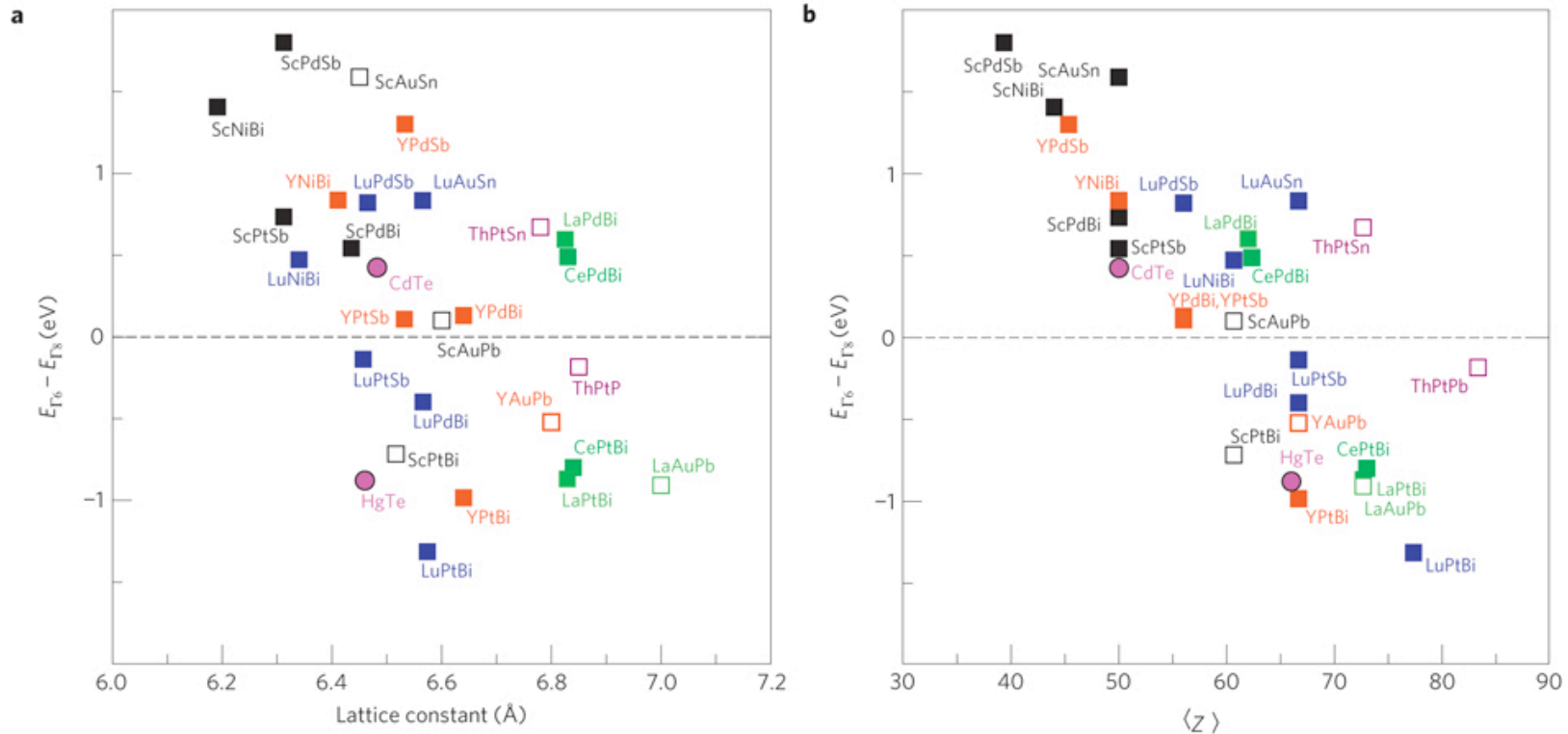
Chadov et al. *Nature Mater.* 9 (2010) 541-545



Red colour marks the bands with Γ_8 symmetry, blue with Γ_6 . Comparison reveals obvious similarity between binary systems and their ternary equivalents: both CdTe and ScPtSb are trivial semiconductors with Γ_6 situated above Γ_8 , which sits at the Fermi energy (set to zero). Both HgTe and ScPtBi are topological with inverted band order; the band with Γ_6 symmetry is situated below Γ_8 .

Tunable multifunctional topological insulators in ternary Heusler compounds

Chadov *et al. Nature Mater.* 9 (2010) 541-545



HgTe and CdTe binaries are shown for comparison. Open squares mark the systems not reported in the literature. (a) $E_{\Gamma_6} - E_{\Gamma_8}$ difference as a function of the lattice constant. The borderline compounds (between trivial and topological) insulators (YPtSb, YPdBi, ScAuPb) are situated closer to the zero horizontal line. (b) $E_{\Gamma_6} - E_{\Gamma_8}$ difference as a function of the average spin-orbit coupling strength represented by the average nuclear charge per formula.