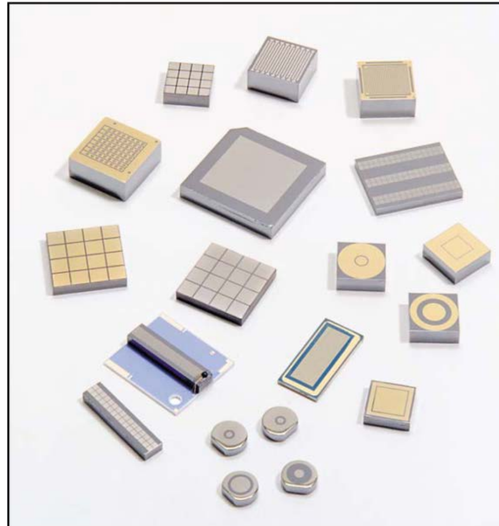
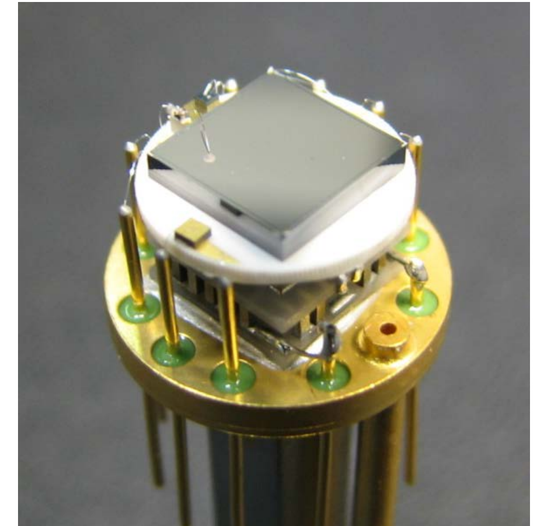
esa

The quest for optimized sensor materials



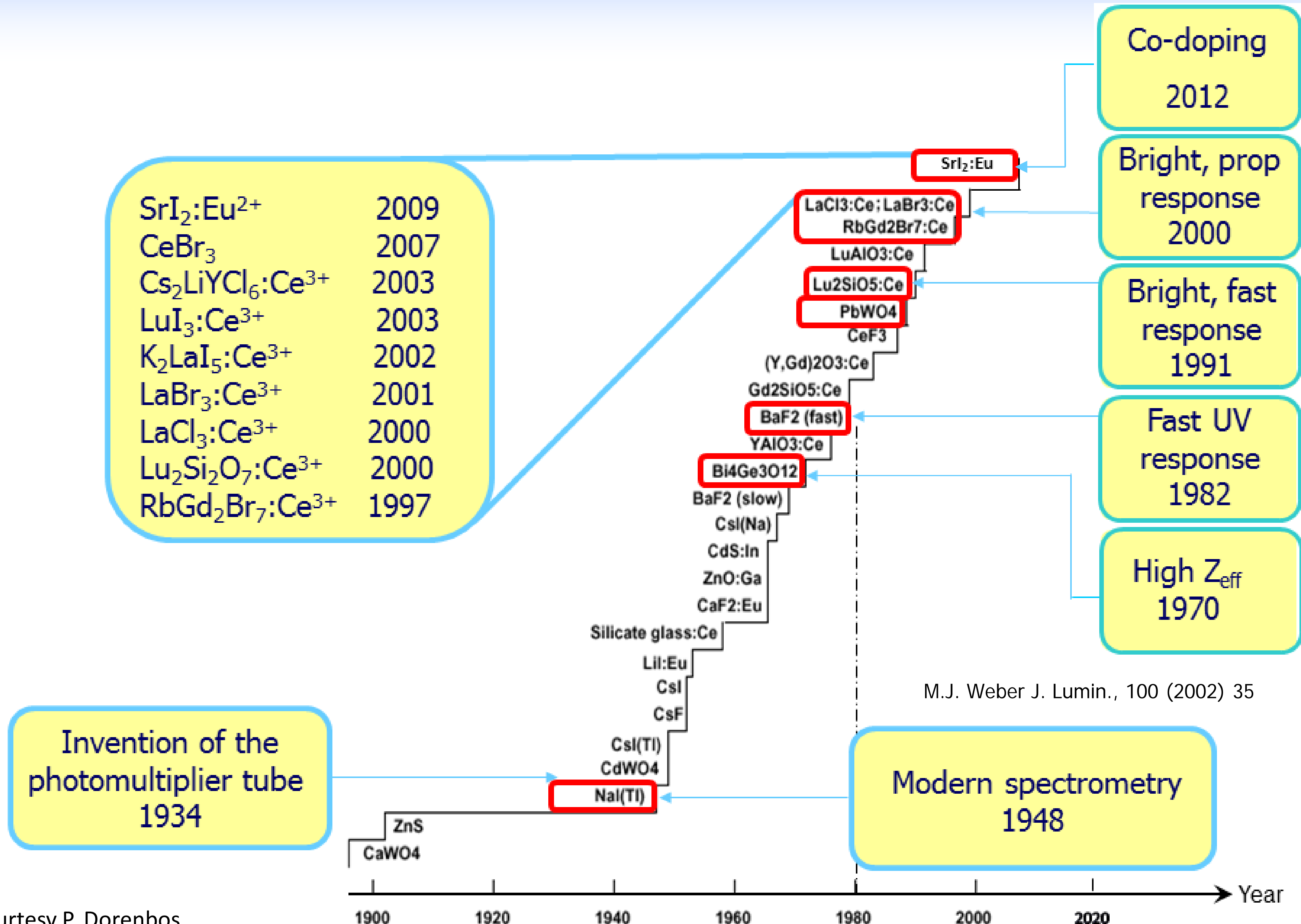


Alan Owens
European Space Agency
Noordwijk, The Netherlands

Outline

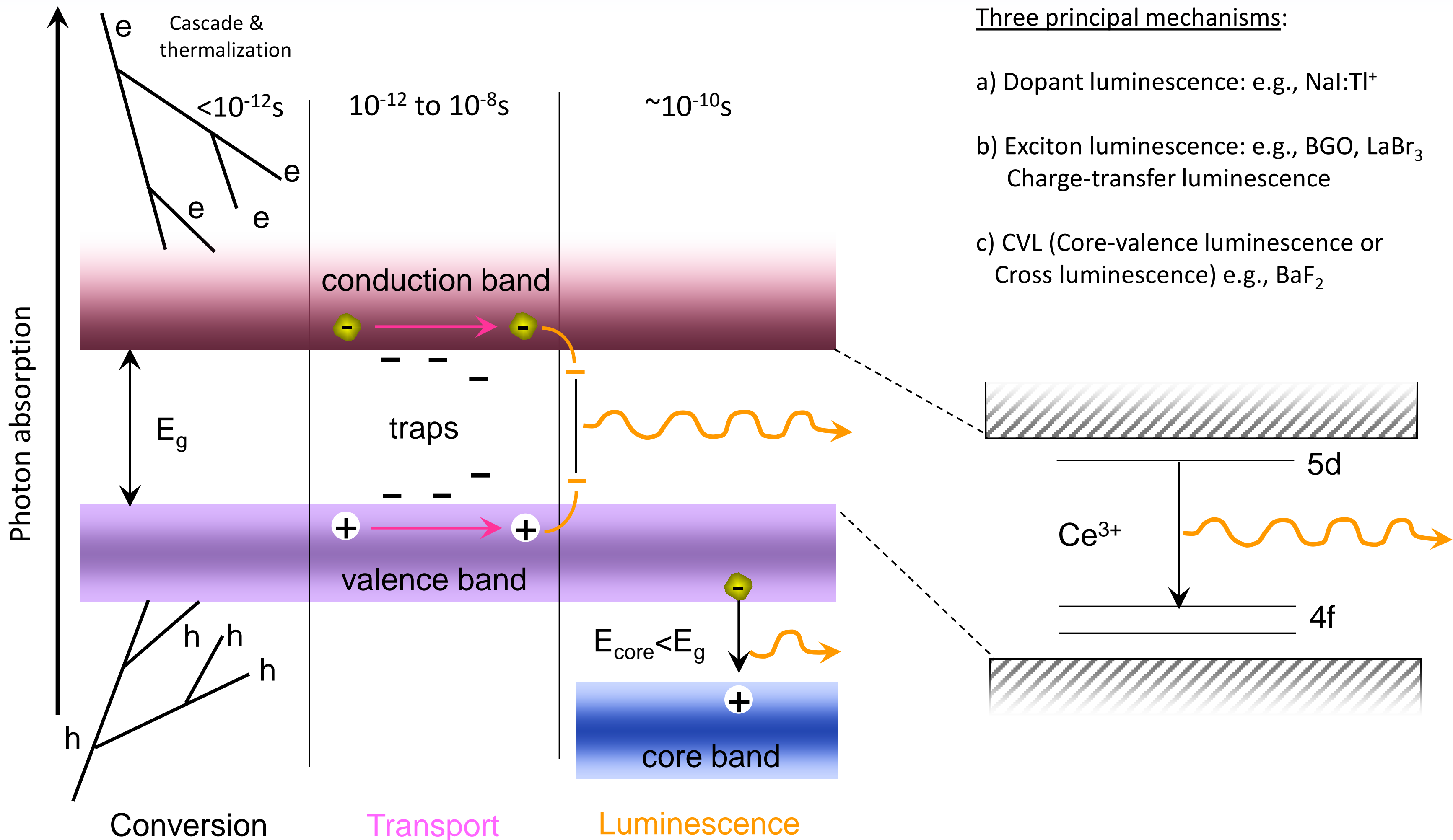
- A brief history
- Semiconductor and scintillator materials
- Detection systems
- Performance limitations
- Improving performance
- New detection techniques

Scintillator development + milestones



Courtesy P. Dorenbos

Scintillation mechanism



Three principal mechanisms:

a) Dopant luminescence: e.g., NaI:Tl^{+}

b) Exciton luminescence: e.g., BGO, $LaBr_3$
Charge-transfer luminescence

c) CVL (Core-valence luminescence or Cross luminescence) e.g., BaF_2

M. Nikl, *Scintillation detectors for X-rays*, Meas. Sci. Technol.,17 (2006) R37.

Scintillating materials

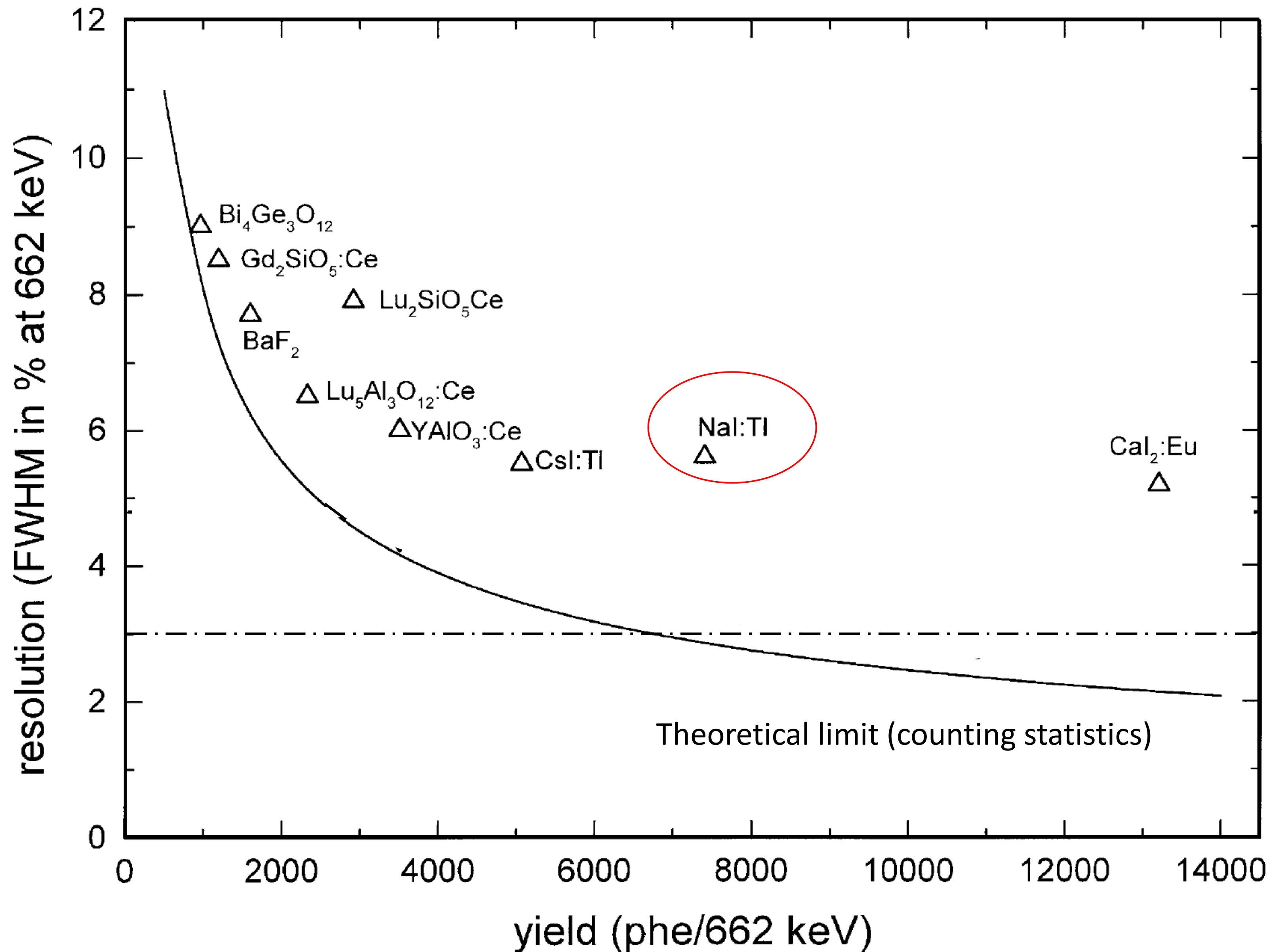
Advantages

- Simple
- Essentially passive
- Radiation hard
- Can be grown in large sizes $\Rightarrow$ area detectors
- Make good gamma-ray detectors $\Rightarrow$ volume

Disadvantages

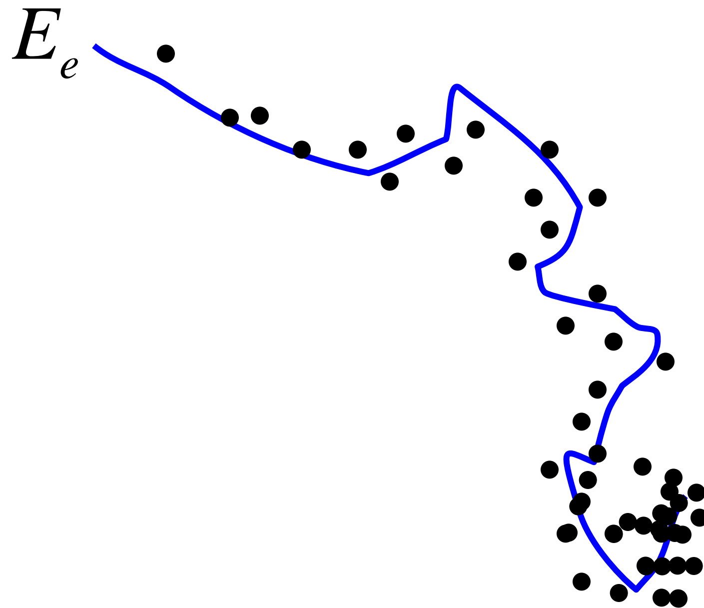
- Non-proportional response
- Limited potential in spatially resolved spectroscopy (Anger cameras?)
- New generation of high resolution scintillators are expensive
- Generally hygroscopic (especially inorganic crystals)
- Requires separate read-out device

But……..



Components of the resolution function

1) R_{stat} - creation of the ionization track



$$N_{eh} = \frac{E}{W_{eh}} = \frac{E_\gamma}{\beta E_g}$$

$$\left.\begin{aligned} \beta &\approx 2.5 \\ E_g &= 5.8\,\text{eV} \end{aligned}\right\} \Rightarrow N_{eh} = 69{,}000 \ \ /\text{MeV}$$

$$\Rightarrow \sigma = \sqrt{N_{eh}}$$

For a 662 keV energy deposition, $\Delta E/E = 1\%$

$R_{\text{stat}} \Rightarrow$ Does not limit resolution

The issue of non-proportionality

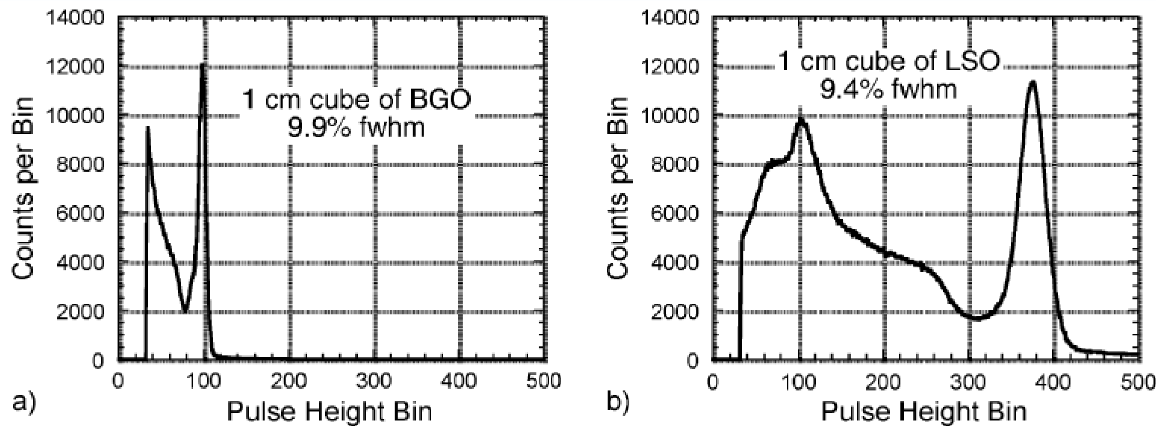


Fig. 1. Pulse height spectra under 662 keV gamma ray excitation. (a) 1 cm cube of BGO. (b) 1 cm cube of LSO.

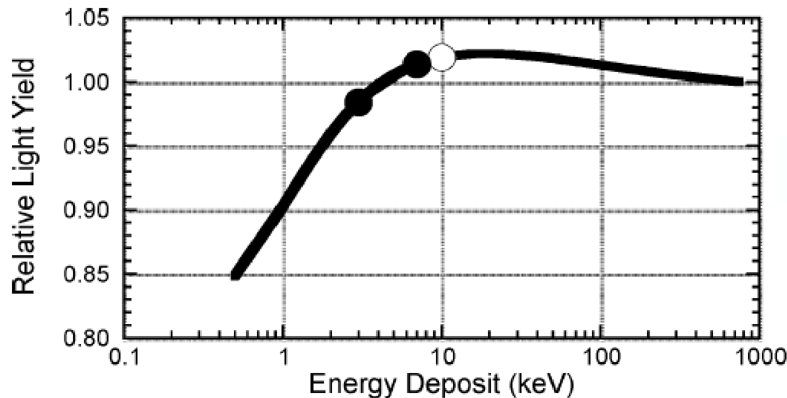


Fig. 2. Photon response curve for a hypothetical scintillator. The y-axis plots the relative light yield (the luminous efficiency, in photons per MeV, normalized to the value at 662 keV) as a function of the energy of the photon that excited it, which is plotted on the x-axis. Deviations from a horizontal line are "non-proportionality," meaning that the luminous efficiency depends on the incident energy.

$E_{\gamma 1}$ = 662 keV→ collection of *n* secondary electrons with energies E_1, E_2, ... E_i, ... E_n. Photon yield $Y(E_i)$ due to electron *i* depends on electron energy.

$E_{\gamma 2}$ = 662 keV→ another collection of *m* secondary electrons with energies E_1, E_2, ... E_j, ...E_m.

$$Y_{\gamma_1} = \sum_{i=1}^{n} Y(E_i) \neq Y_{\gamma 2} = \sum_{j=1}^{m} Y(E_j)$$

From Moses, IEEE Trans. Nucl. Sci., **55** (2008) 1049-1053

Factors determining the energy resolution, *R*

- Statistics in the number of detected photons, N_{stat}
- Non-proportional response of the scintillator, N_{np}
- Inhomogeneities in the crystal, light reflection, or photocathode, N_{inh}
- Contributions from the statistics in the gain of the PMT or electronic noise in (A)PDs, N_{det}

$$R^2 = R_{stat}^2 + R_{np}^2 + R_{inh}^2 + R_{\mathrm{det}}^2$$

7.8% 2.0% 7.0% 1.0% 3.0%

Contributions at 662 keV for a 1 inch RCC NaI(Tl) xtal + PMT

Scintillator activities - ESA specific requirements

Produce a large volume gamma-ray detector with:

- High γ-ray detection efficiency in the MeV region, ε_p> 14% @ 1 MeV

  Achieve through use of high density materials (i.e., > 5 g cm^{-3})

- High energy resolution better than 3% FWHM @ 662 keV

  Achieve using scintillation materials with high light output (>50,000 ph/MeV) – require low light non-proportionality, low readout noise (< 20 phe rms)

Inferred from the BepiColombo SCI-RD

- Environmentally robust

  Hardness > 2 Mho, Radiation tolerance > 1 Mrad, 10^4 Gy, low activation susceptibility (< 3 ct cm^{-3} s^{-1}),

  Achieve using low phosphorescence inorganic scintillators, radiation damage mitigation via annealing possibility *via* thermal or optical bleaching means

- Inert

  Room or elevated temperature operation (-10°C to +50°C), no special EMC, cleanliness or handling requirements, no moving parts

- Minimally resourced

  No services (e.g., cooling, vacuum, calibration sources, radiation or magnetic shielding), no maintenance, 4 kg, 4W, 1 L – above all simple

Towards the next generation - candidate materials

Goal - scintillator with 3% or better energy resolution at 662 keV. The selection of candidate materials for gamma ray spectroscopy is relatively straightforward since they must be formed out of elements (shown encircled below) which are,

1) high-Z_{eff} (equivalent or higher than $LaBr_3$)

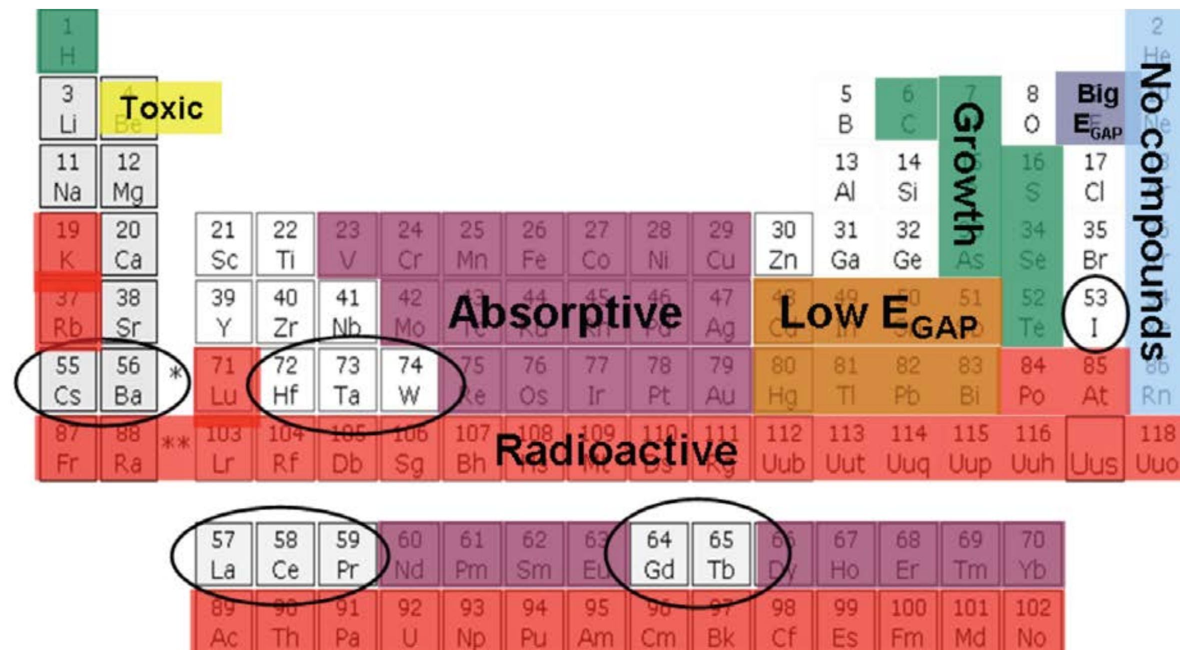
2) that are not radioactive,

3) that are not optically absorptive,

4) have a band gap that $1 eV < \varepsilon_g < 10$ eV, (good statistics)

5) focus on binary alkaline earth halides (high light outputs)

6) it must be possible to grow the candidate material in stable form (low ΔG_f - Gibbs free energy of formation)



Cherepy et al. IEEE Trans. Nucl. Sci., **NS-56** (2010) pp. 873-880

Candidate materials

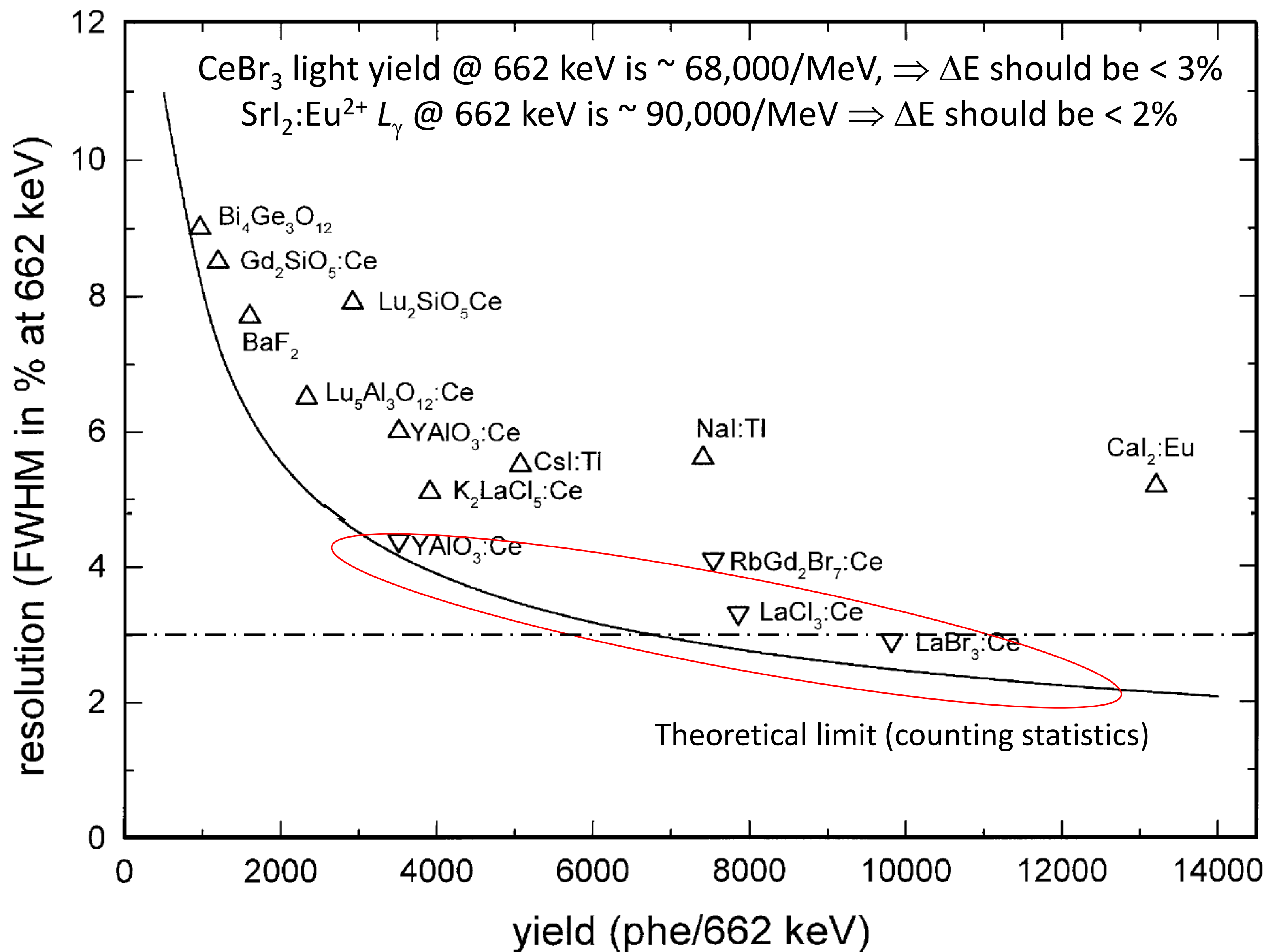
Compound	Light Yield, Photons/MeV	Peak emission (nm)	Decay time (ns)	nPr $1\text{-}\sigma_{PR}$	Figure of merit
$PbWO_4$	250	590	98	0.93	
$Bi_4Ge_3O_{12}$ (BGO)	8000	480	300	0.91	
BaF_2	10000	310	620	0.97	
Lu_2SiO_5:Ce (LSO)	30000	420	40	0.78	
$Lu_{1.8}Y_{0.2}SiO_5$:Ce (LYSO)	34000	397	41	0.89	
NaI:Tl	45000	415	230	0.85	
CsI:Tl^+	56000	550	980	0.86	
LaCl:Ce^{3+}	48000	350	28	0.94	98
$LaBr_3$:Ce^{3+}	75000	380	30	0.95	111

Figure of merit based on a modified form of minimum sensitivity in the presence of a background equations given in Cooper and Chupp.

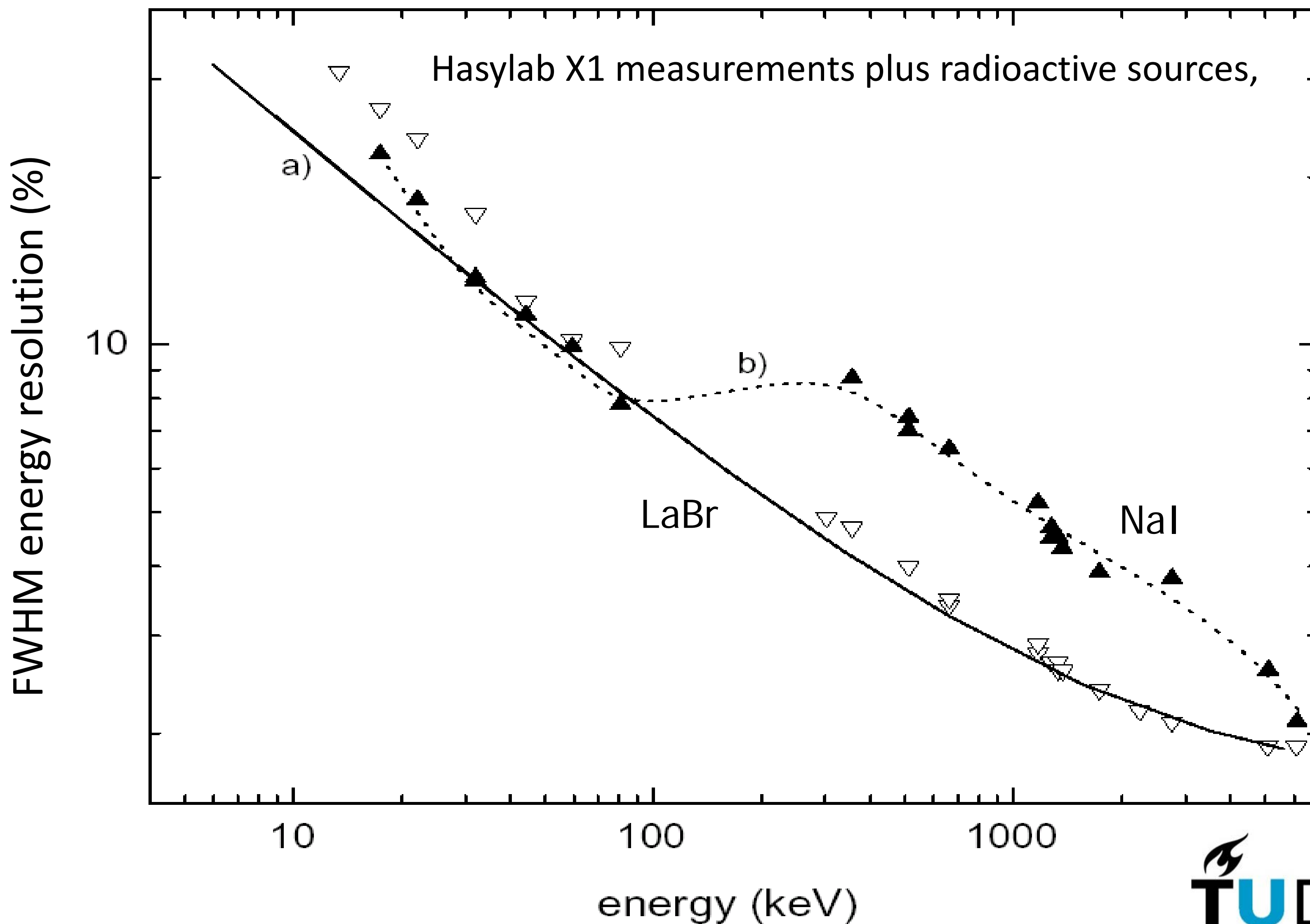
Does not take into account nPr

J.A. Cooper, “Factors Determining the Ultimate Sensitivity of Ge(Li) Gamma-Ray Spectrometers”, Nucl. Instr. and Meth., **82** (1970) 273.
E.L. Chupp, “Gamma Ray Astronomy (Nuclear Transition Region)”, D. Reidel Publishing Company, Dordrecht, Holland (1976)

The cerium doped halides

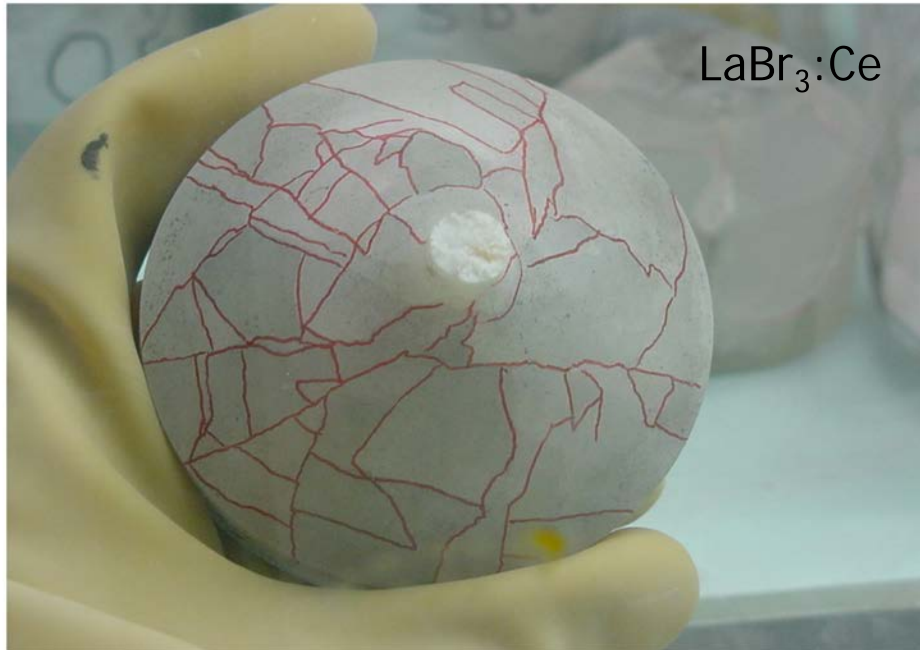


Energy resolution NaI:Tl, $LaBr_3$:0.5% Ce^{3+} vs Energy



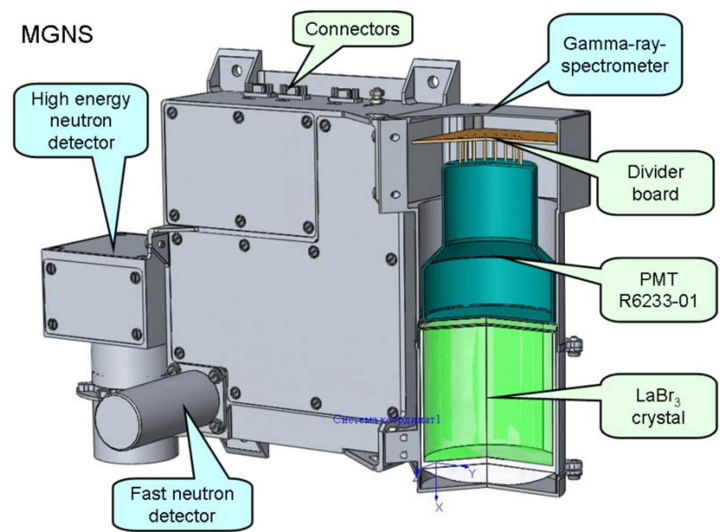
Current project crystal growth capabilities

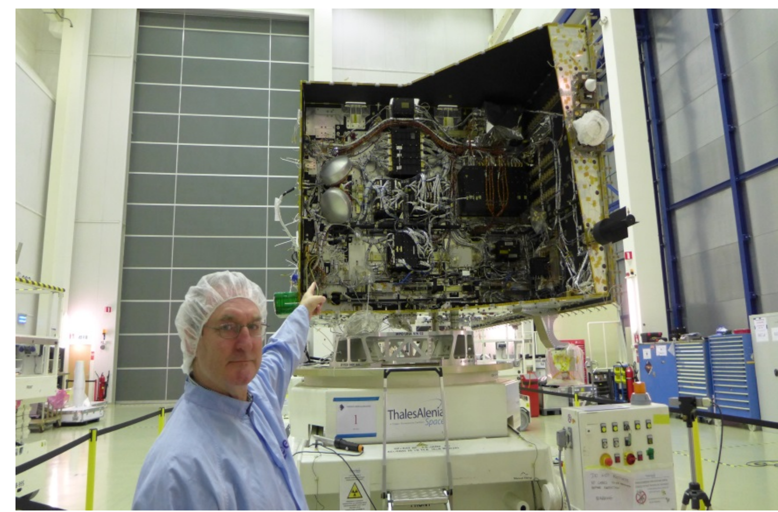
Crystal growth at St Gobain, France/Hëllma Materials, Jena, Germany



Output of the XBr_3 scintillator development program

$LaBr_3$ (10% Ce) gives the best energy resolution. For a 3 inch RCC, ΔE is 3% FWHM at 662 keV. The intrinsic background level is 1 Bq cm^{-3}. Two 2 inch xtals were flown onboard Phobos Grunt. The three inch xtal on BepiColombo has been swapped-out with a 3 inch 4.5% $CeBr_3$ xtal during final integration





IEAP High energy gamma-ray source, chlorine configuration

3x3 inch $LaBr_3$, 3x3 inch NaI(Tl), 6.5 cm HPGe, uniform illumination

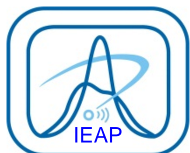
518 Cl + 511
789 Cl
1165 Cl
1470 La
2223 H
2864 Cl
3062 Cl
4980 Cl
5091 Cl D.E.
5205 Cl S.E.
5715 Cl
5601 Cl S.E. + 5600 Cl D.E.
6111 Cl + *6110 Cl S.E.
6620 Cl
6904 Cl S.E.
7414 Cl
7790 Cl
8579 Cl

Count rate (s^{-1})
100
10
1
0.1

Energy (keV)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

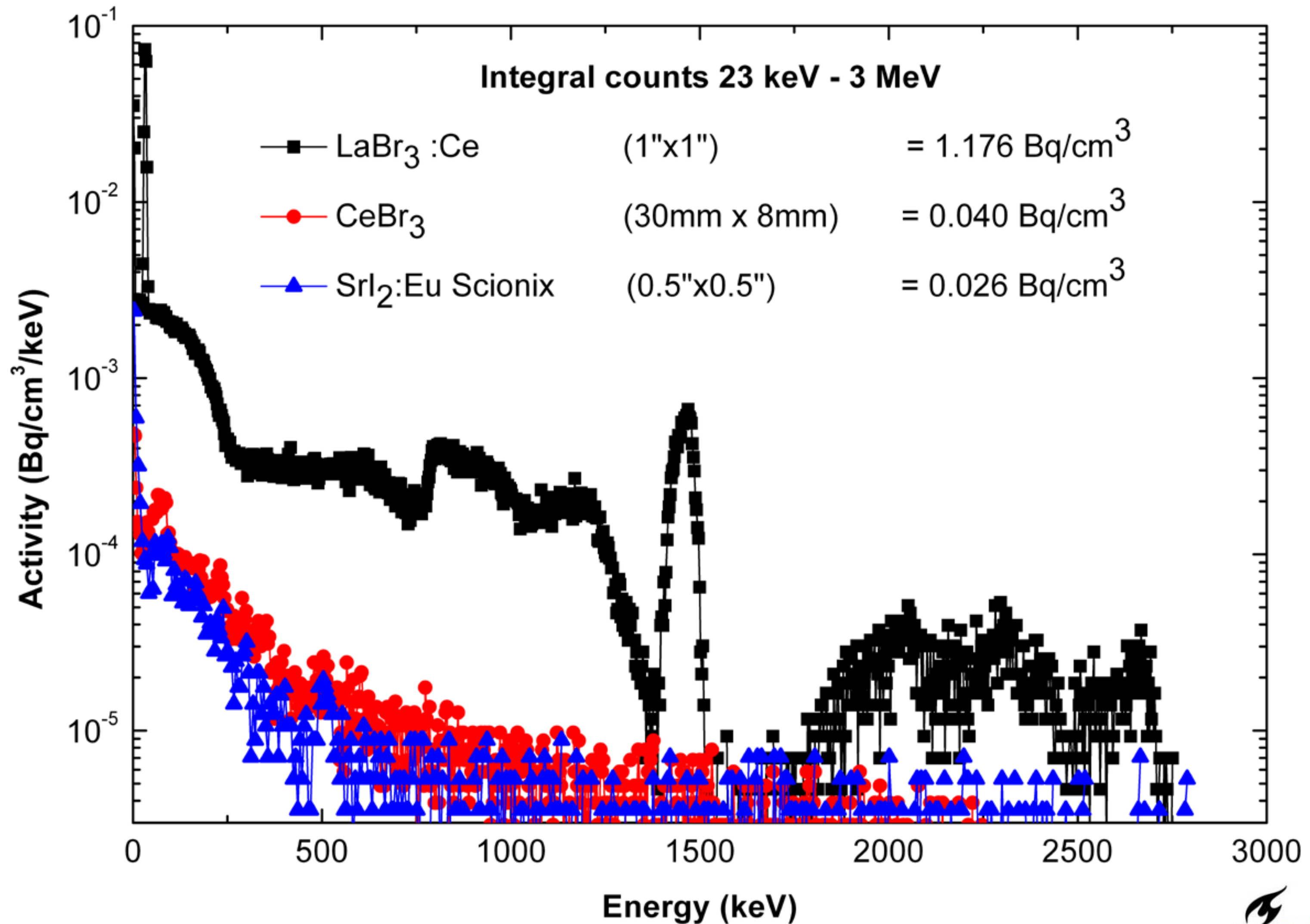
NaI
LaBr3
HPGe

S.E. - Single Escape
D.E. - Double Escape



Intrinsic activity measurements of candidate materials

Measured in lead castle at TU Delft with low ^{40}K PMT. $LaBr_3$ used as benchmark



TU Delft

New candidate materials short list

Compound	Light Yield, Photons/MeV	Peak emission (nm)	Decay time (ns)	nPr $1\text{-}\sigma_{PR}$	Figure of merit
$LaCl:Ce^{3+}$	48000	350	28	0.94	98
$LaBr_3:Ce^{3+}$	75000	380	30	0.95	111
$Cs_2LiLaBr_6:Ce$ (CLLB)	60000	410	270	0.95?	169
$Gd_3Sc_2Al_3O_{12}:Ce$ (GYGAG)	48000	570	100	0.99?	827
$CeBr_3$	68000	370	17	0.93	596
$SrI_2:Eu^{2+}$	90000	430	1200	0.98	1045

Figure of merit based on a modified form of minimum sensitivity in the presence of a background equations given in Cooper and Chupp.

Does not take into account nPr

J.A. Cooper, “Factors Determining the Ultimate Sensitivity of Ge(Li) Gamma-Ray Spectrometers”, Nucl. Instr. and Meth., **82** (1970) 273.
E.L. Chupp, “Gamma Ray Astronomy (Nuclear Transition Region)”, D. Reidel Publishing Company, Dordrecht, Holland (1976)

The way forward – REE-doping – but what scintillator?

Given that Ce^{3+}, Pr^{3+} and Eu^{2+} are the current activator workhorse. The choice of scintillator is driven by aspects of the 5d-4f decay scheme.

$\Rightarrow$ For Ce doping, the light yield limit of 100-130 ph/keV and decay time limit of 15-17 ns has been approached

$\Rightarrow$ For Pr doping, a reduction in decay time from 20 ns-10 ns is still possible

$\Rightarrow$ For both Pr and Eu larger light yields are still possible

Condition for room temperature stable 5d-4f emission:

$E5d < E_{cb} - 0.5$ eV, otherwise trapping occurs

$E4f > E_{vb} + 0.5$ eV otherwise quenching occurs

* For Ce^{3+} doping the optimum material has a light yield of 100-130 ph/keV a BG of 3-4 eV and a decay time of 20 ns

* For Pr^{3+} doped scintillators, the optimum material has a LY of 65-80 ph/keV and a bandgap 5-6 eV and a decay time of 10 ns

* For Eu^{2+} doped scintillators, the optimum material has a LY of 105-140 ph/keV and a bandgap 2.8-3.8 eV

Work carried out at TU Delft

The way forward – co-doping

- Sr co-doping of $LaBr_3$ has achieved a ΔE of 2% at 662 keV
- Sr co-doping of $CeBr_3$ has achieved a ΔE of 3% at 662 keV

Semiconductor materials

Advantages

- Wide variety of compounds available
- Compounds can be selected for specific environments
- Materials can be engineered for specific applications
- Electronics can be integrated – e.g. DEPFET
- Very good for spatially resolved spectroscopy applications

Disadvantages

- Requires hyperpure material - expensive
- Usually requires cooling for best performance
- Difficult to grow in large sizes - not good for area detectors
- Radiation damage issues

Forming compounds

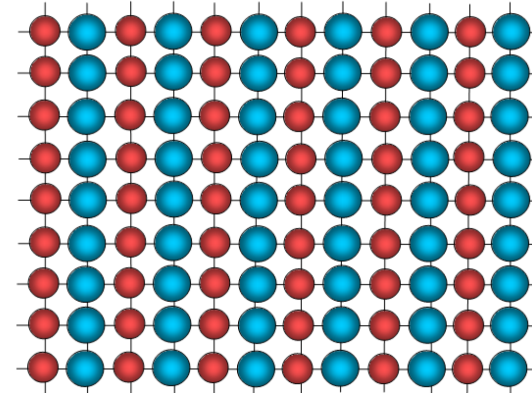
Follow the Hume-Rothery rules

- The ***atomic radii*** of the different atoms involved must ***differ by less than 15%***

- The components must have the ***same crystal structure***

- The species must have ***similar valences***

- The components must ***have similar electronegativities***



Rational

- Atomic radii must be similar because if substituted atom is too large, considerable strain will develop in crystal lattice

- The components must have similar crystal structure if solubility is to occur over all proportions, e.g., the CdTe-ZnTe system. However, this is less important if small proportions of solute being added - such as in the doping of semiconductors.

- Similar valences and electronegativities indicates that components have similar bonding properties.

W. Hume-Rothery, *The Structure of Metals and Alloys,* The Institute of Metals, London (1969).

Is the compound semiconducting?

Mooser-Pearson laws

Materials will show semiconducting properties if they obey the following rules:

1) The bonds are predominantly covalent.

2) The bonds are formed by a process of electron sharing which leads to completely filled ***s*** and ***p*** sub-shells on all atoms in elemental semiconductors. For compound semiconductors, the condition has to apply for each constituent element.

3) The presence of vacant "metallic" orbital's on some atoms in a compound will not prevent semiconductivity *provided* that these atoms are not bonded together.

4) The bonds form a continuous array in one, two or three dimensions throughout the crystal.

Elements from groups IV to group VII will satisfy conditions 1 and 2. Compounds which follow the second condition can be represented by the following expression†.

$$n_e / n_a + b = 8$$

Here, n_e is the number of valence electrons per molecule, n_a is the number of group IV to VII atoms per molecule and b is the average number of covalent bonds formed by one of these atoms with other atoms of groups IV to VII. Thus, for GaAs, n_e=8, n_a=1 and b=0 – which equals 8.

Bottom line for binaries, the group numbers should add up to 8 – i.e., group I-VII, III-V, IV-IV, II-VI and I-VII

†Equivalent to the 8-N rule

E. Mooser, W.B.Pearson, "*The Chemical Bond in Semiconductors*", J. Electron., Vol.**1** (1956) pp. 629-645

Deriving new semiconductors

elemental — IVB — Ge, Si, C

Group

binary — IV-IV — SiGe, SiC

binary — III-V — InP, GaAs, GaN

binary — II-VI — HgTe, CdSe, ZnS

binary — I-VII — AgCl, AgBr, CuCl

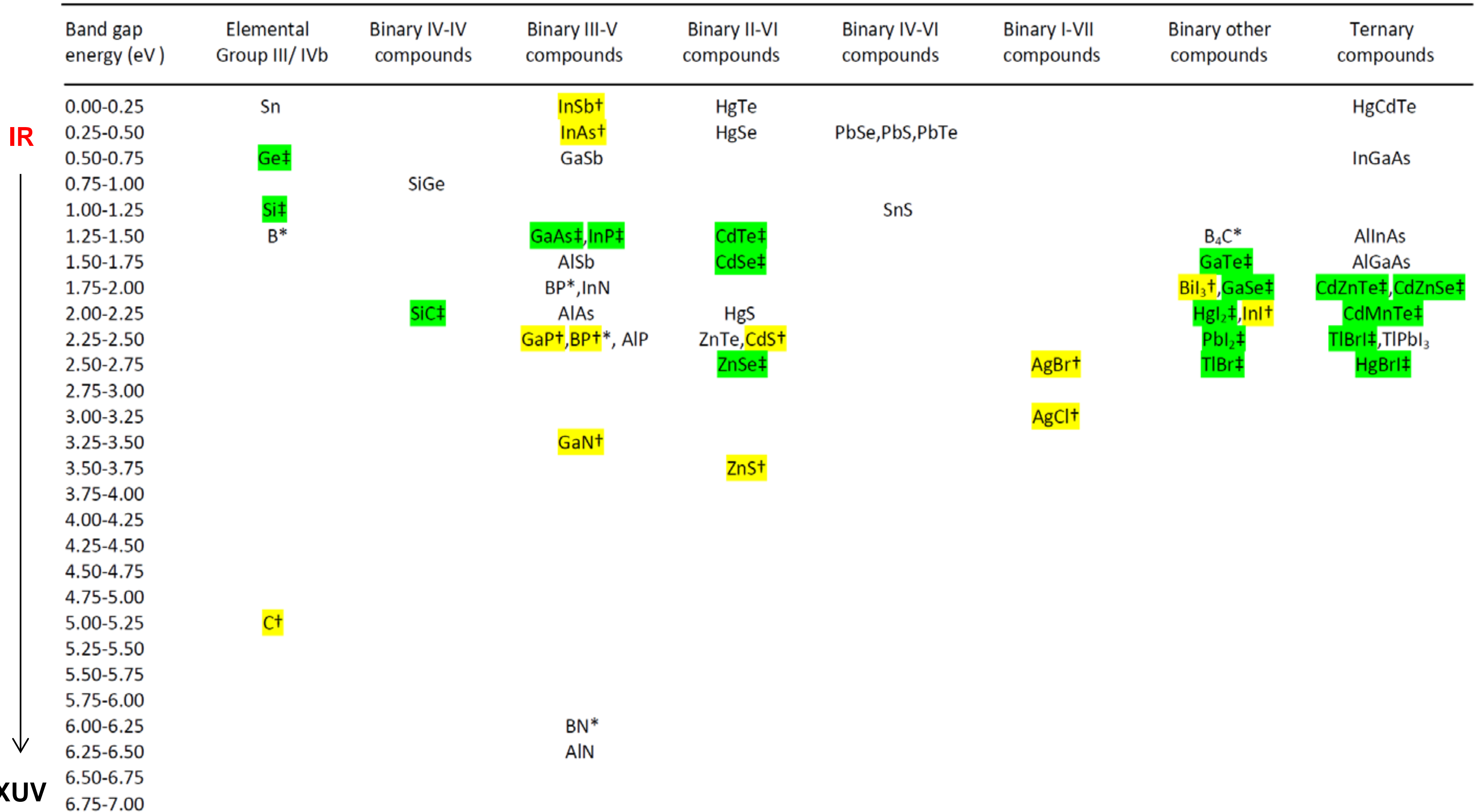
ternary — all — HgCdTe, AlGaAs

quaternary — all — InGaAsP, InGaAlP

Elemental semiconductors essentially limited to C, Si and Ge

What has been looked at?

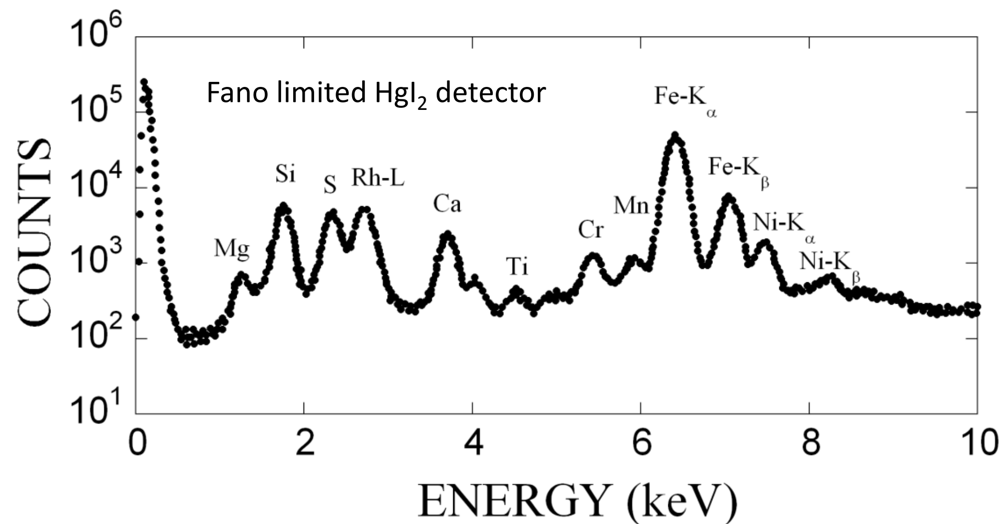
Compound semiconductor material listed by group and in order of increasing band-gap energy ranging from near IR to XUV wavelengths



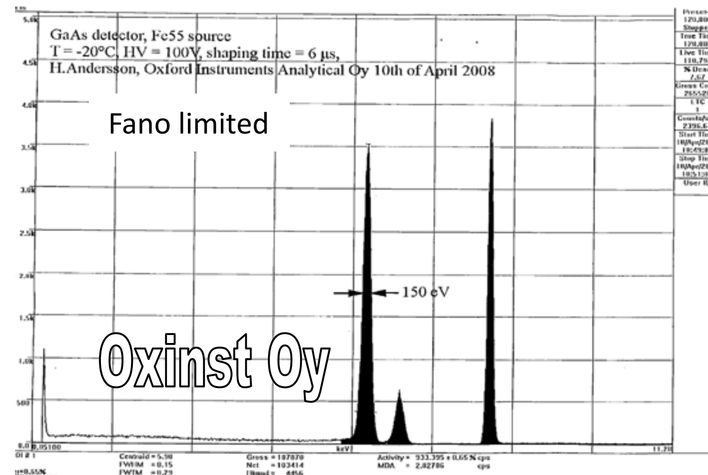
Band gap energy (eV)	Elemental Group III/ IVb	Binary IV-IV compounds	Binary III-V compounds	Binary II-VI compounds	Binary IV-VI compounds	Binary I-VII compounds	Binary other compounds	Ternary compounds
0.00-0.25	Sn		InSb†	HgTe				HgCdTe
0.25-0.50			InAs†	HgSe	PbSe,PbS,PbTe			
0.50-0.75	Ge‡		GaSb					InGaAs
0.75-1.00		SiGe						
1.00-1.25	Si‡				SnS			
1.25-1.50	B*		GaAs‡,InP‡	CdTe‡			B_4C*	AlInAs
1.50-1.75			AlSb	CdSe‡			GaTe‡	AlGaAs
1.75-2.00			BP*,InN				BiI_3†,GaSe‡	CdZnTe‡,CdZnSe‡
2.00-2.25		SiC‡	AlAs	HgS			HgI_2‡,InI†	CdMnTe‡
2.25-2.50			GaP†,BP†*, AlP	ZnTe,CdS†			PbI_2‡	TlBrI‡,$TlPbI_3$
2.50-2.75				ZnSe‡		AgBr†	TlBr‡	HgBrI‡
2.75-3.00								
3.00-3.25						AgCl†		
3.25-3.50			GaN†					
3.50-3.75				ZnS†				
3.75-4.00								
4.00-4.25								
4.25-4.50								
4.50-4.75								
4.75-5.00								
5.00-5.25	C†							
5.25-5.50								
5.50-5.75								
5.75-6.00								
6.00-6.25			BN*					
6.25-6.50			AlN					
6.50-6.75								
6.75-7.00								

†Compounds which have shown a response to energetic radiation. ‡Materials for which spectroscopic measurements (i.e. $\Delta E/E>1$) have been made at X-ray wavelengths.*Investigated for n detection.

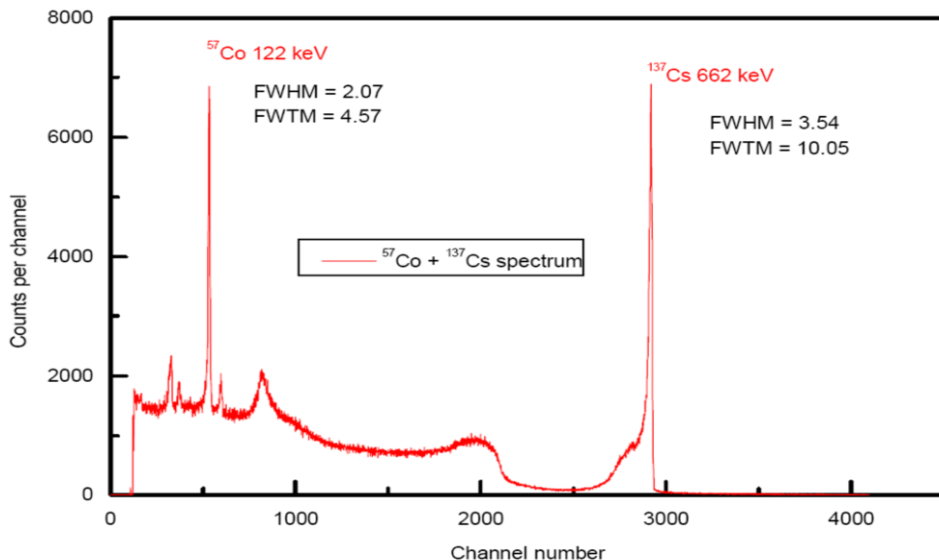
Some of the best spectroscopic results



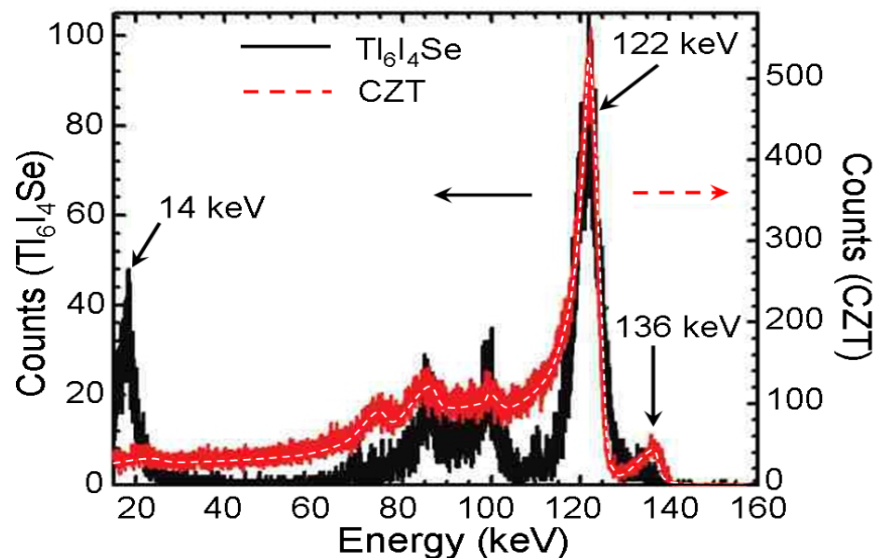
HgI_2 5 mm², 200 µm thick detector at 0°C. ΔE at 5.9 keV =198 eV (Iwanczyk *et al.* 1989)



GaAs 0.5 x 0.5 x 0.2mm³ detector at -20°C. ΔE at 5.9 keV =150 eV (courtesy S. Nennonen)

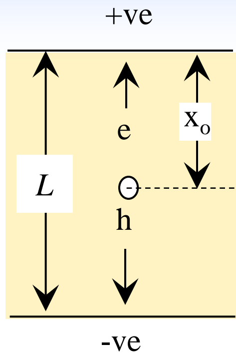


CdTe 1cm², 2.1 mm thick detector cooled to –35°C. ΔE at 662 keV was 3.5 keV (Khusainov et al. 1999).



Tl_6I_4Se, 6×4×2 mm³ detector. ΔE at 122 keV = 5.7 keV (Johnsen *et al.* 2011)

These results only apply to small thin detectors, because.....



Charge transport described by the Hecht relation

$$CCE = \frac{Q}{Q_o} = \frac{\lambda_e}{L}\left[1-\exp\left(-\frac{L-x_o}{\lambda_e}\right)\right] + \frac{\lambda_h}{L}\left[1-\exp\left(-\frac{x_o}{\lambda_h}\right)\right]$$

λe	
1 m	Si
1 cm	CZT
1 mm	GaAs
1 μm	GaP

$$\lambda_e = \mu_e \tau_e E \qquad \lambda_h = \mu_h \tau_h E$$

but μτ's rarely over 10^{-4}cm^{2}V^{-1} and E usually < 10^4 Vcm^{-1}

For λ/L <1 there will be a position dependence in the collected charge and spectral broadening

For the general case of $\lambda_e \neq \lambda_h$, the relative broadening is given by

$$\left(\frac{\sigma_c^2}{E}\right)^2 = \frac{2\lambda_e^2\lambda_h^2}{L^3(\lambda_e-\lambda_h)}\left(e^{-L/\lambda_e}-e^{-L/\lambda_h}\right) - \frac{1}{L^4}\left[\lambda_e^2\left(e^{-L/\lambda_e}-1\right)+\lambda_h^2\left(e^{-L/\lambda_h}-1\right)\right]^2$$

$$-\frac{\lambda_e^3}{2L^3}\left(e^{-2L/\lambda_e}-1\right) - \frac{\lambda_h^3}{2L^3}\left(e^{-2L/\lambda_h}-1\right)$$

Bottom line - spectroscopy dominated by the carrier with the poorest transport properties

Iwanczyk et al., Nucl. Instr. and Meth., Vol., **A322** (1992) 421

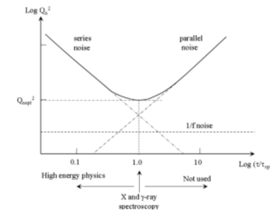
CCE and spectral broadening

Three main noise components comprise the resolution function ΔE

Fano noise

$$F = \frac{\sigma_{\exp}^2}{var_{\text{poisson}}} \quad \Rightarrow \quad \sigma_{\text{F}}^2 = FE\varepsilon$$

For RC-RC shaping



Electronic noise

$$\Delta e = \frac{2.355\,\varepsilon\,\text{ENC}}{e}$$

$$ENC^2 = \left(\frac{\varepsilon^2}{8}\right)\left[\left(2eI + \frac{4kT}{R_b}\right)\tau + \left(4kTR_s + v_{na}^2\right)C_d^2\frac{1}{\tau} + 4A_f C_d^2\right]$$

current noise (parallel) — voltage noise (series) — 1/f noise

Charge trapping noise

$$\left(\frac{\sigma_{\text{c}}^2}{E}\right)^2 = \frac{2\lambda_e^2\lambda_h^2}{L^3(\lambda_{\text{e}} - \lambda_{\text{h}})}\left(\text{e}^{-L/\lambda_{\text{e}}} - \text{e}^{-L/\lambda_{\text{h}}}\right) - \frac{1}{L^4}\left[\lambda_{\text{e}}^2\left(\text{e}^{-L/\lambda_{\text{e}}} - 1\right) + \lambda_{\text{h}}^2\left(\text{e}^{-L/\lambda_{\text{h}}} - 1\right)\right]^2 - \frac{\lambda_{\text{e}}^3}{2L^3}\left(\text{e}^{-2L/\lambda_{\text{e}}} - 1\right) + \frac{\lambda_{\text{h}}^3}{2L^3}\left(\text{e}^{-2L/\lambda_{\text{h}}} - 1\right)$$

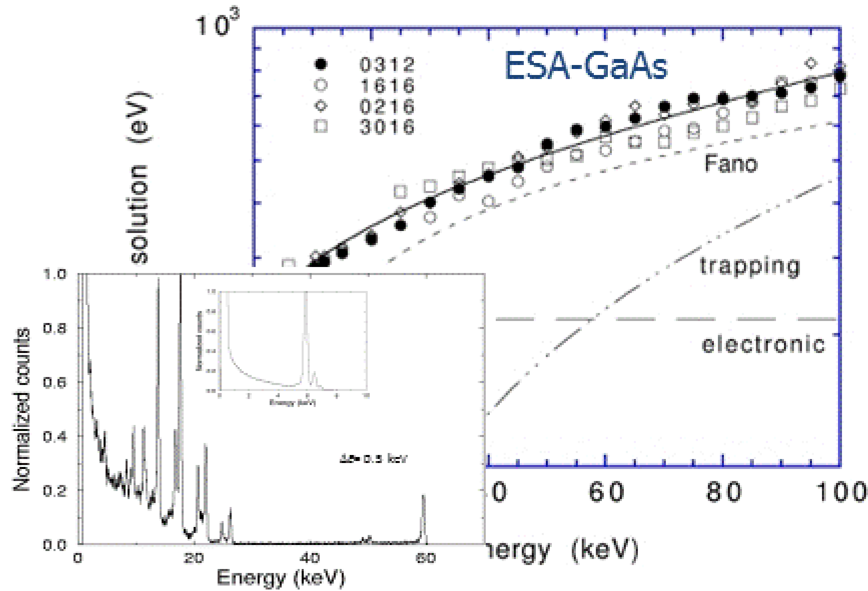
$$\Delta E = f(\sigma_{\text{F}}^2, \sigma_{\text{e}}^2, \sigma_{\text{c}}^2)$$

$$\Delta E = 2.355\sqrt{F\varepsilon E_{\text{o}} + \left(\Delta e / 2.355\right) + a_1 E_{\text{o}}^{a2}}$$

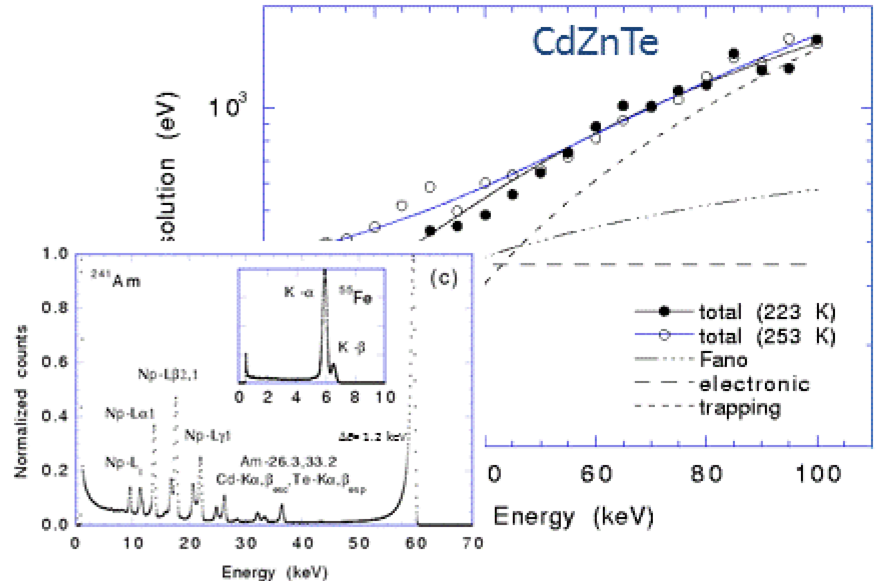
assuming all components are normally distributed

Effect of $\mu\tau$ on performance – smaller the $\mu\tau$ the poorer the performance or thinner the detector

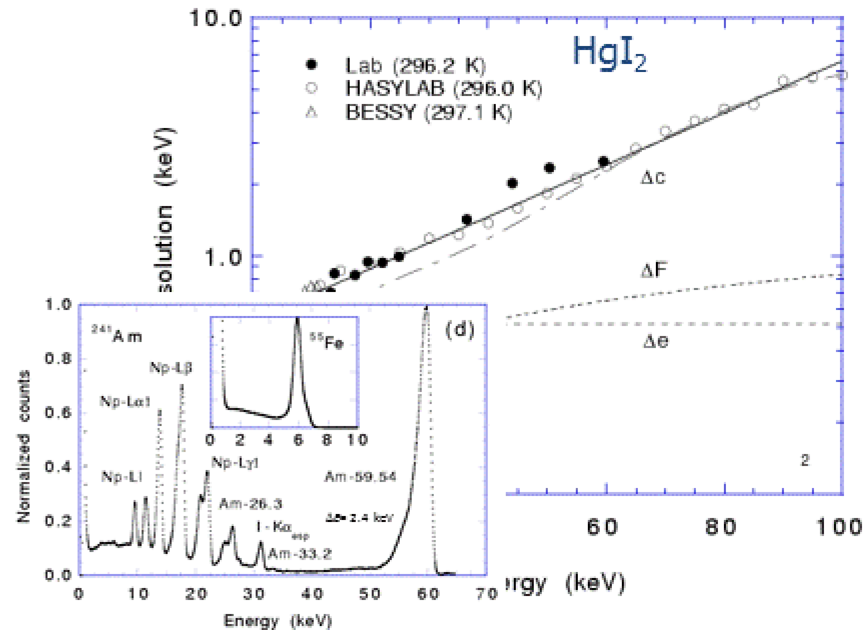
$\mu\tau \sim 10^{-2} \Rightarrow$ Fano limited



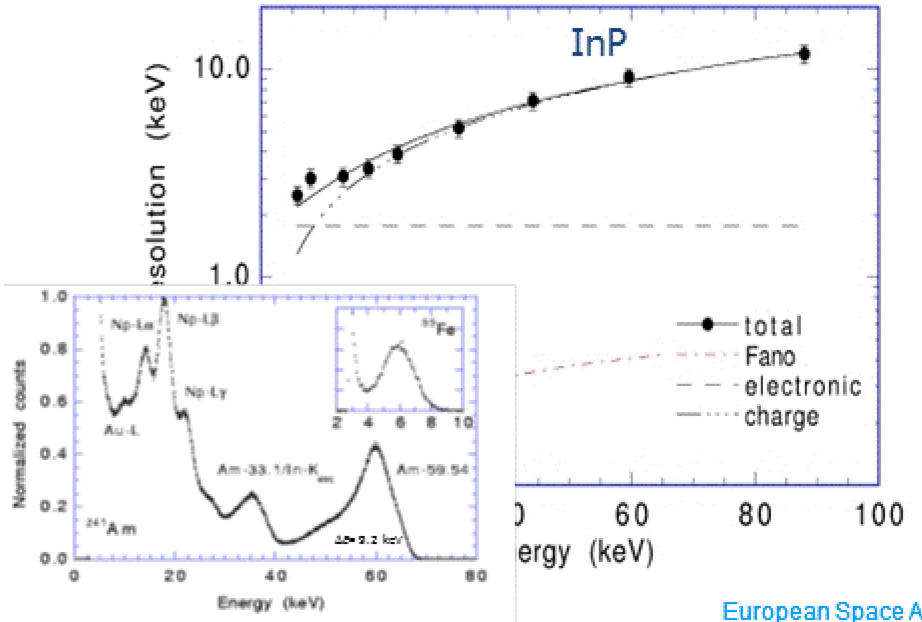
$\mu\tau \sim 10^{-3} \Rightarrow$ partially Fano limited



$\mu\tau \sim 10^{-4} \Rightarrow$ not Fano limited



$\mu\tau \sim 10^{-5} \Rightarrow$ what's Fano limited ?



European Space Agency

esa

Performance limiting effects

1) Poor transport parameters

2) Crystal purity/stoichiometry

3) Thermal effects

4) Polarization

5) Radiation effects

Transport properties III-V, II-VI compounds

esa

Group III-V Materials

Physical Properties – Group III-V Materials

Material	Crystal Structure	Pearson symbols/ Space /Point group	Lattice constants a or a, c (nm)	Atomic numbers	Av. Mol. weight	Density (g cm^{-3})	Melting point (K)	Iconicity f_i	KH (kg mm^{-2})
InSb	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.648	49, 51	236.6	4.78	797	0.321	220
InAs	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.606	49, 33	189.7	4.68	1210	0.357	430
InP	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.587	49, 15	145.8	4.79	1335	0.421	460
InN	W	hP4, P6_3mc(C_{6v}^4)	0.354, 0.870	49, 7	128.8	6.81	2146	0.578	1140
GaSb	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.610	31, 51	191.5	5.61	991	0.261	450
GaAs	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.564	31, 33	144.6	5.32	1513	0.310	750
GaP	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.545	31, 15	100.7	4.14	1730	0.327	964
β-GaN	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.451	31, 7	83.7	6.15	3246[2]	0.500	1830
α-GaN	W	hP4, P6_3mc(C_{6v}^4)	0.319, 0.518	31, 7	83.7	6.07	2791	0.500	1200-1700
BAs	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.478	5, 33	85.7	5.22	2027	0.044	1937
BP	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.4538	5, 15	41.8	2.97	3300	0.032	3263
β-BN	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.362	5, 7	24.8	3.48	3246	0.256	6730-7648
α-BN	H	hP4, P6_3/mmc(D_{6h})	0.250, 0.666	5, 7	24.8	3.28	2873[2]	0.221	1489
AlSb	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.614	13, 51	148.7	4.22	1338	0.250	408
AlAs	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.566	13, 33	101.9	3.76	1710	0.274	510
AlP	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.546	13, 15	58.0	2.36	2823	0.307	561
AlN	W	hP4, P6_3mc(C_{6v}^4)	0.311, 0.498	13, 7	41.0	3.26	3487	0.449	1020-1427

[1](॥) = parallel to c axis, (⊥) perpendicular to c axis
[2]sublimes/decomposes

Electronic Properties – Group III-V Materials

Material	Type	Bandgap (eV)	Pair Energy (eV)	$\varepsilon_r(0)$[1]	Resistivity (Ω-cm)	Electron Mobility (cm^{2}V^{-1}s^{-1})	Hole Mobility (cm^{2}V^{-1}s^{-1})	$\mu_e\tau_e$ (cm^{2}V^{-1})	$\mu_h\tau_h$ (cm^{2}V^{-1})
InSb	D	0.18	1.2	17.7	~100 @ 4K	80000	1250	7×10^{-5}	
InAs	D	0.354	2.0	15.1	0.03	33000	460		
InP	D	1.34	4.2	12.4	10^8	4600	150	2×10^{-5}	1×10^{-5}
InN	D	1.89*		13.1(⊥), 14.4(॥)		3200	<80		
GaSb	D	0.75		15.7	0.04	4000	700	1.4×10^{-5}	
GaAs	D	1.425	4.35	13.1	10^{10}	8500	400	1×10^{-4}	4×10^{-6}
GaP	I	2.27	6.5	11.1	10^8-10^{11}	110	75	1.4×10^{-6}	
β-GaN	D	3.23		8.9	10^6	760	250		
α-GaN	D	3.42		10.4(⊥), 9.5(॥)	>10^{10}	1500	30		
BAs	I	1.85**		9.9					
BP	I	2.4	6.5	11.0	20	30-120	285-500		
BN (c)	I	6.4		7.1	10^5	<200	<500		
BN (h)	I	5.2		7.04(⊥), 5.1(॥)	10^{14}				
AlSb	I	1.62	6.58	14.4	0.04-10^7	200	420		
AlAs	I	2.15		10.9	0.2	200	100		
AlP	I	2.42		9.8	1×10^{-5}	60	450		
AlN (h)	D	6.19		8.3(⊥), 8.9(॥)	10^{13}	300	14		

* Early studies showed 1.9-2.05. A recent study claims a value of 0.7-0.8 [33] and is supported by measurement [34].
**Calculated value [35]. Optical absorption measurements suggest a bandgap energy of 0.67 eV [36].

Group II-VI Materials

Physical Properties – Group II-VI Materials

Material	Crystal Structure	Pearson symbols/ Space /Point group	Lattice Constants a or a, c (nm)	Atomic Numbers	Av. Mol. Weight	Density (g cm^{-3})	Melting point (K)	Iconicity f_i	KH (kg mm^{-2})
HgTe	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.646	80, 52	328.2	8.12	943	0.650	23.5-37.7
HgSe	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.609	80, 34	279.6	8.22	1270	0.680	23.5
α-HgS	W	hP6,P6_3mc(C_{6v})	0.415, 0.950	80, 16	232.7	8.19	1093	0.790	91
β-HgS	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.585	80, 16	232.7	7.73	857	0.790	138[a]
CdTe	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.648	48, 52	240.0	5.85	1366	0.675	45.9-61.2
CdSe (c)	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.607	48, 34	191.4	5.67	1512	0.699	130
CdSe	W	hP4,P6_3mc(C_{6v}^4)	0.430, 0.701	48, 34	191.4	5.81	2023	0.699	91.8
CdS (c)	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.582	48, 16	144.5	4.87	1748	0.685	125
CdS (h)	W	hp4, P6_3mc(C_{6v})	0.414, 0.671	48, 16	144.5	4.83	1748	0.685	123-235
ZnTe	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.610	30, 52	193.0	6.34	1568	0.609	61.2-91.8
ZnSe (c)	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.567	30, 34	144.3	5.26	1799	0.630	139.7-186.6
β-ZnS	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.541	30, 16	97.5	4.08	1991[b]	0.623	178
α-ZnS	W	hP4, P6_3mc(C_{6v}^4)	0.382, 0.626	30, 16	97.5	4.08	2196	0.623	178
ZnO	ZB	cF8, F$\bar{4}$3m(T_d^2)	0.463	30, 8	81.4	5.68	2248	0.616	5.0 (M[c])
ZnO	W	hP4,P6_3mc(C_{6v}^4)	0.3250, 0.5204	30, 8	81.4	5.61	1975[b]	0.616	407.9[d]
β-MgTe	W	hp4, P6_3mc(C_{6v})	0.4530, 0.7406	25, 52	151.9	3.81	1360	0.554	143
β-MgSe	NaCl	cF8, Fm$\bar{3}$m(O_h^5)	0.589	12, 34	103.3	4.20	1560	0.790	152
β-MgS	NaCl	cF8, Fm$\bar{3}$m(O_h^5)	0.520	12, 16	56.4	2.86	2783	0.786	3.5 (M[c])[e]

[a]estimated
[b]decomposes/sublimes
[c]Mohs scale
[d]hardest of the II-VI compounds
[e]value given for its mineral form, niningerite

Electronic Properties – Group II-VI Materials

Material	Type	Bandgap (eV)	Pair Energy (eV)	Dielectric Constant $\varepsilon_r(0)$[a]	Resistivity (Ω-cm)	Electron Mobility (cm^{2}V^{-1}s^{-1})	Hole Mobility (cm^{2}V^{-1}s^{-1})	$\mu_e\tau_e$ (cm^{2}V^{-1})	$\mu_h\tau_h$ (cm^{2}V^{-1})
HgTe	SM	-0.14		20.8	10^{-2}-10^{-3}	25000	350		
HgSe	SM	-0.06		25.6		20000	2		
α-HgS	D	2.03		23.5(॥), 18.2(⊥)	3450 (॥), 11080 (⊥)	30(॥), 10(⊥)			
β-HgS	SM	0.54		18.2		250			
CdTe	D	1.48	4.43	10.4	10^9	1050	100	3.3×10^{-3}	2×10^{-4}
CdSe (c)	D	1.74	5.5	10.0	10^5	800	50	7.2×10^{-4}	7.5×10^{-5}
CdSe (h)	D	1.75	5.5	9.3(⊥), 10.2(॥)	10^8	840	75	6×10^{-5}	7.5×10^{-5}
CdS (c)	D	2.42	6.3	5.4		340	50		
CdS (h)	D	2.51	7.8	8.3(⊥), 8.7(॥)	10^{10}	330	48	10^{-7}	
ZnTe	D	2.28	7.0	10.4	10^{10}	340	100	1.4×10^{-6}	7×10^{-5}
ZnSe (c)	D	2.63	8.0	9.2	2×10^9	540	28	4×10^{-5}	
β-ZnS (c)	D	3.58	8.2	8.9	10^{10}	165	10		
α-ZnS (w)	D	3.91		8.6(⊥), 8.4(॥)	10^8-10^{12}	280(॥), 165(⊥)	100-800		
ZnO (c)	D	3.35	7.5	9.0		200	180		
ZnO (w)	D	3.37		7.8(⊥), 8.8(॥)	10^9	250(॥), 280(⊥)	125		
β-MgTe	D	3.49		6.1					
β-MgSe	D	4.05		5.2					
β-MgS	D	4.5 (77K)		4.5					

A. Owens, Compound Semiconductor Radiation Detectors, CRC Press (2012).

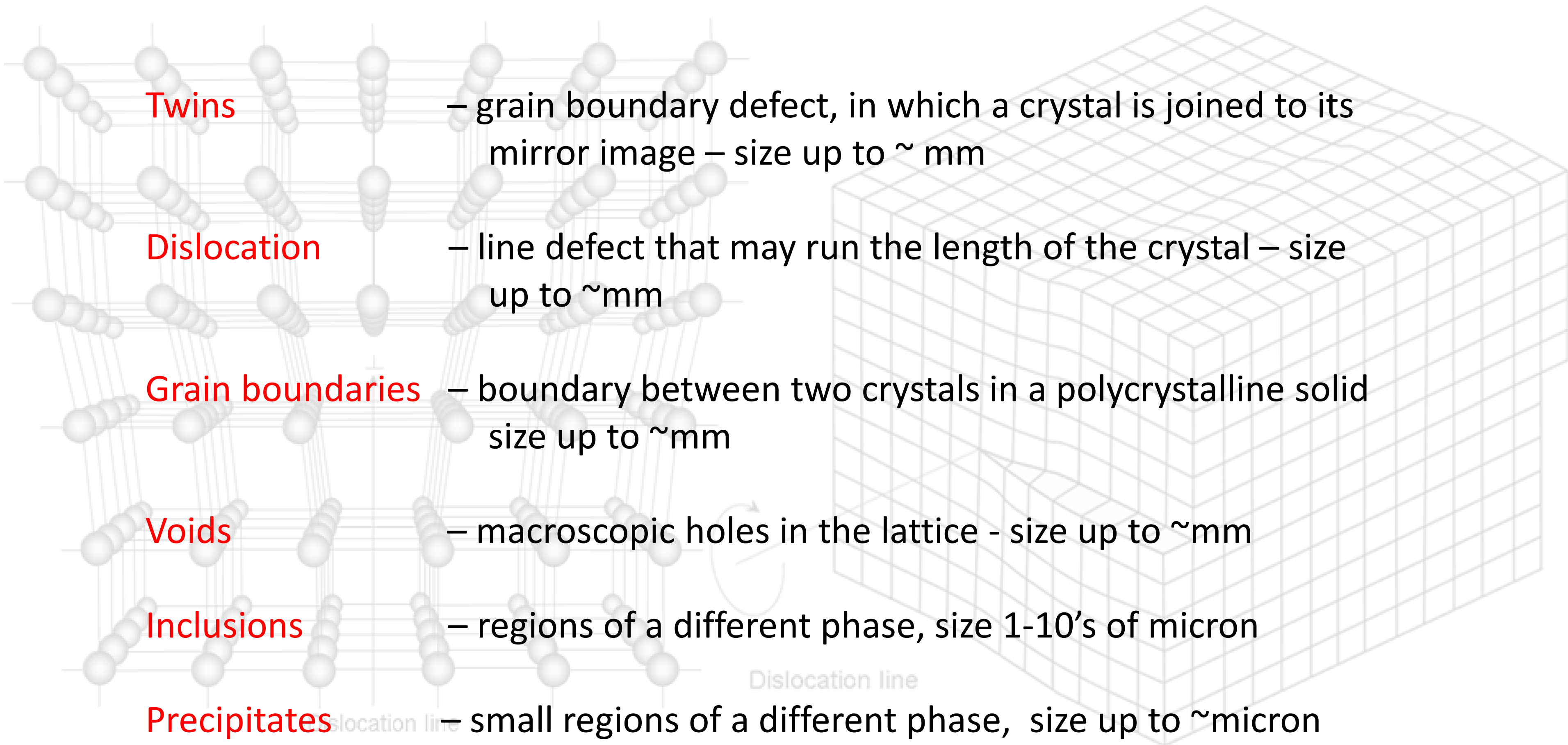
The usual suspects

Room temperature properties of wide band gap compound semiconductor materials suitable for hard X- and γ-ray detectors. The abbreviations are: C = Czochralski, LEC = Liquid Encapsulated Czochralski, THM = Traveller Heater Method, BM = Bridgman Method, HPB = High Pressure Bridgman and VA=Vertical Ampoule Method.

Material	Growth method	Atomic Number	Density (g/cm^3)	Band gap (eV)	Epair (eV)	Resist-ivity (Ω-cm)	$\mu\tau$(e) Product (cm^2/V)	$\mu\tau$ (h) Product (cm^2/V)
Si	C	14	2.33	1.12	3.6	10^4	4×10^{-1}	2×10^{-1}
Ge	C	32	5.33	1.57	4.6	50	1	1
GaAs	CVPE	31,33	5.32	1.43	4.2	10^{11}	10^{-2}	5×10^{-4}
InP	LEC	15.49	4.78	1.43	4.2	10^6	5×10^{-6}	$< 2\times10^{-5}$
CdTe	THM	48,52	6.2	1.44	4.4	10^9	3×10^{-3}	2.6×10^{-4}
$Cd_{0.9}Zn_{0.1}Te$	HPB	48,30,52	5.78	1.57	4.6	10^{11}	7×10^{-3}	9×10^{-5}
PbI_2	BM	82,53	6.2	2.3-2.6	4.9	10^{12}	8×10^{-6}	9×10^{-7}
HgI_2	VAM	80,53	6.4	2.13	4.2	10^{13}	10^{-4}	4×10^{-5}
TlBr	BM	81,35	7.56	2.68	6.5	10^{12}	3×10^{-5}	1.5×10^{-6}

For compounds, hole $\mu\tau$ is usually 10 times less than electron $\mu\tau$

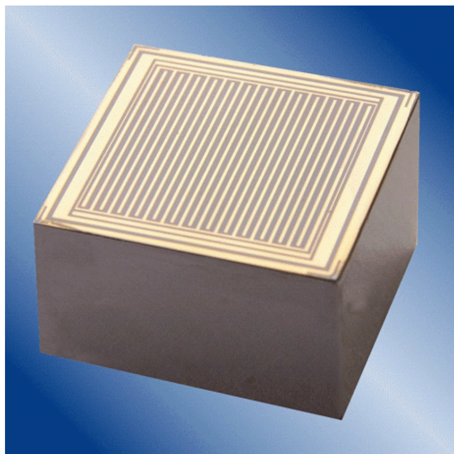
Performance limiting effects
2) Crystal purity/stoichiometry - crystal defects

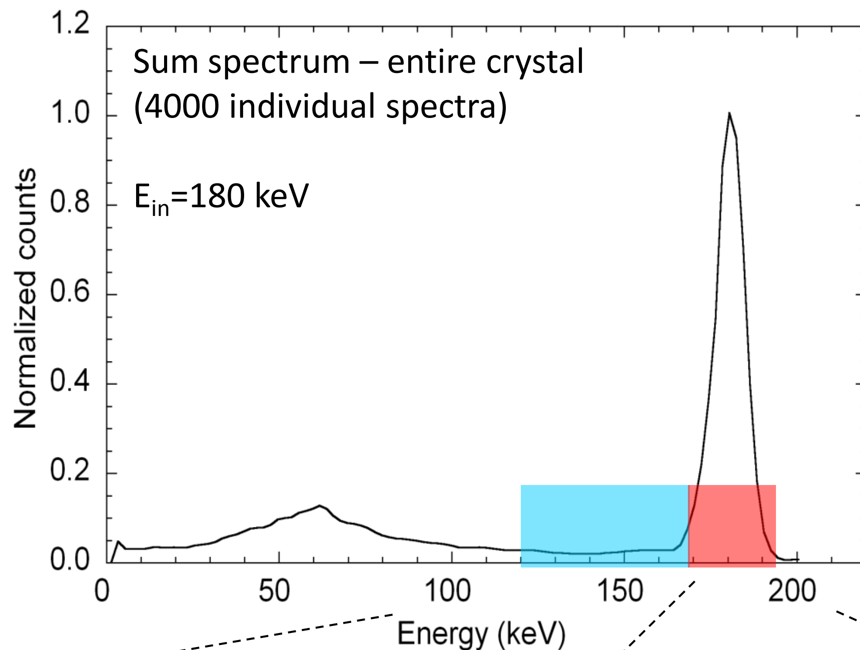


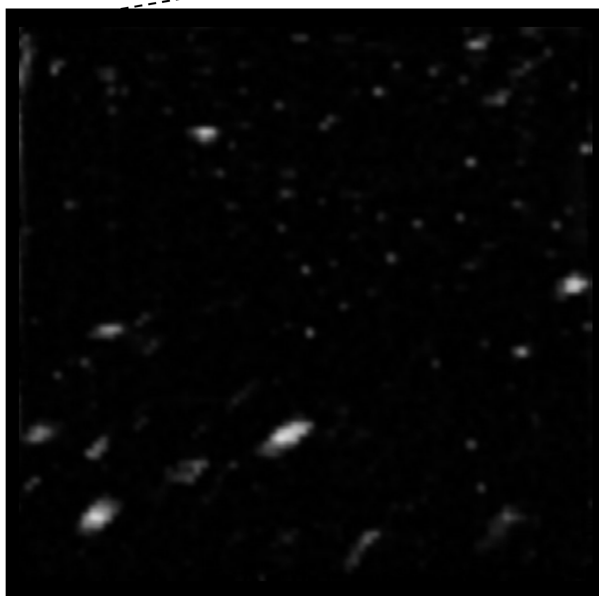
Twins	– grain boundary defect, in which a crystal is joined to its mirror image – size up to ~ mm
Dislocation	– line defect that may run the length of the crystal – size up to ~mm
Grain boundaries	– boundary between two crystals in a polycrystalline solid size up to ~mm
Voids	– macroscopic holes in the lattice - size up to ~mm
Inclusions	– regions of a different phase, size 1-10's of micron
Precipitates	– small regions of a different phase, size up to ~micron

Effects of inclusions on spectra

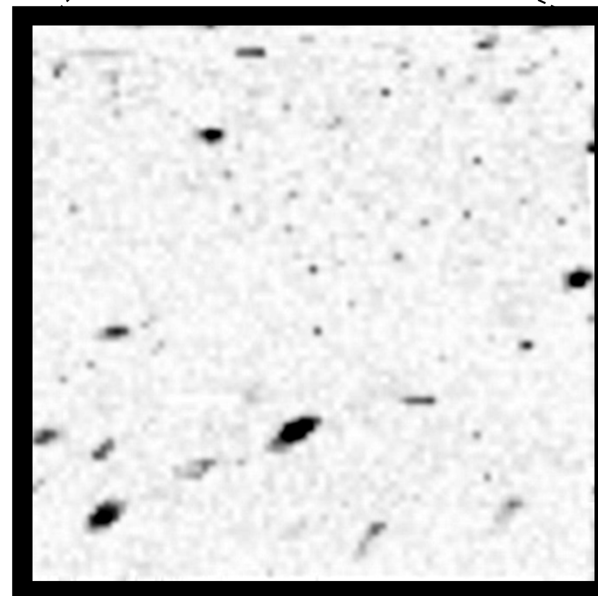
ESRF beamline ID15







Counts between 120-170 keV

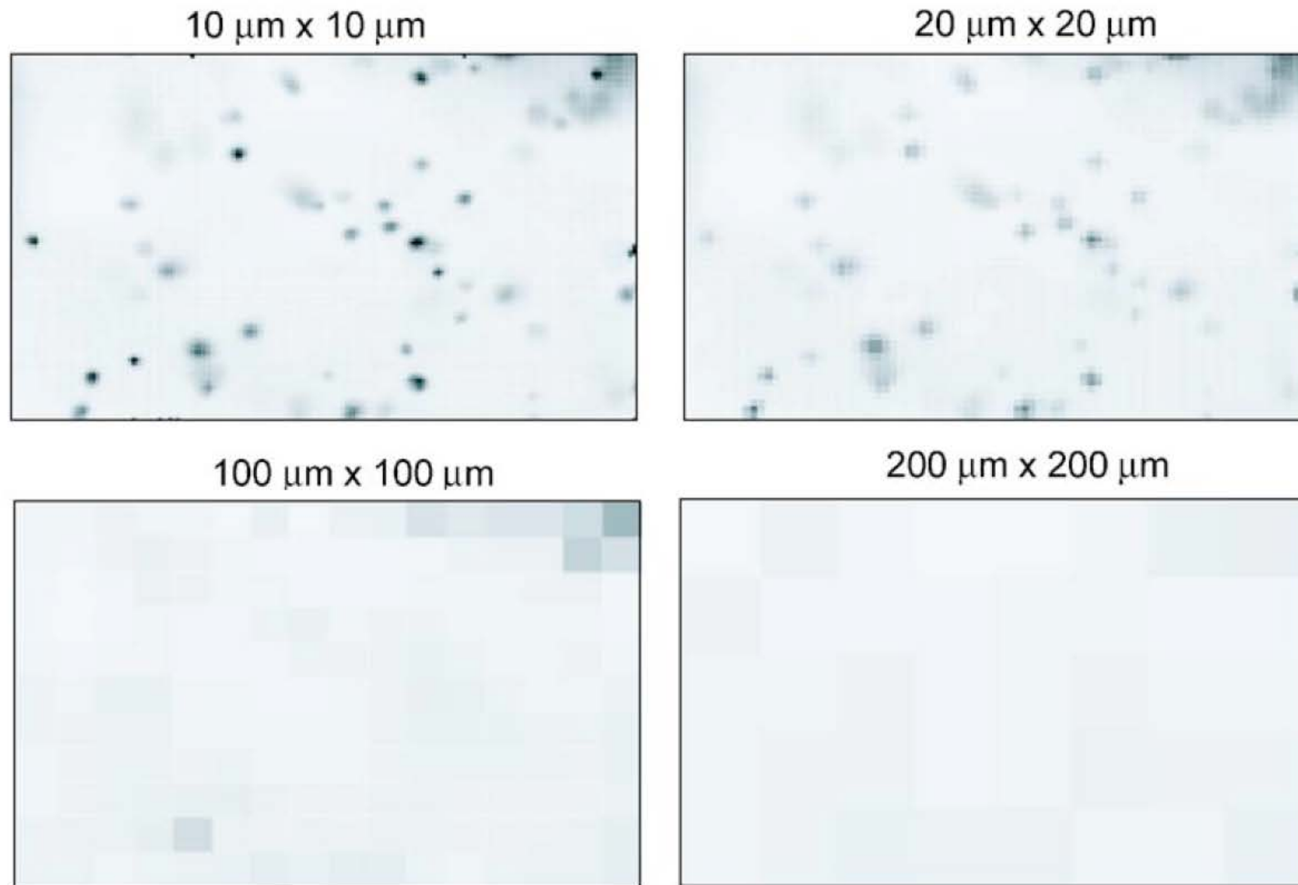


Counts between 170-193 keV

Coplanar grid CZT crystal imperfections

Crystal defects – precipitates and inclusions

Why do some detectors have worse CCE and resolution than other similar detectors?
The X-ray world with finer spatial resolution



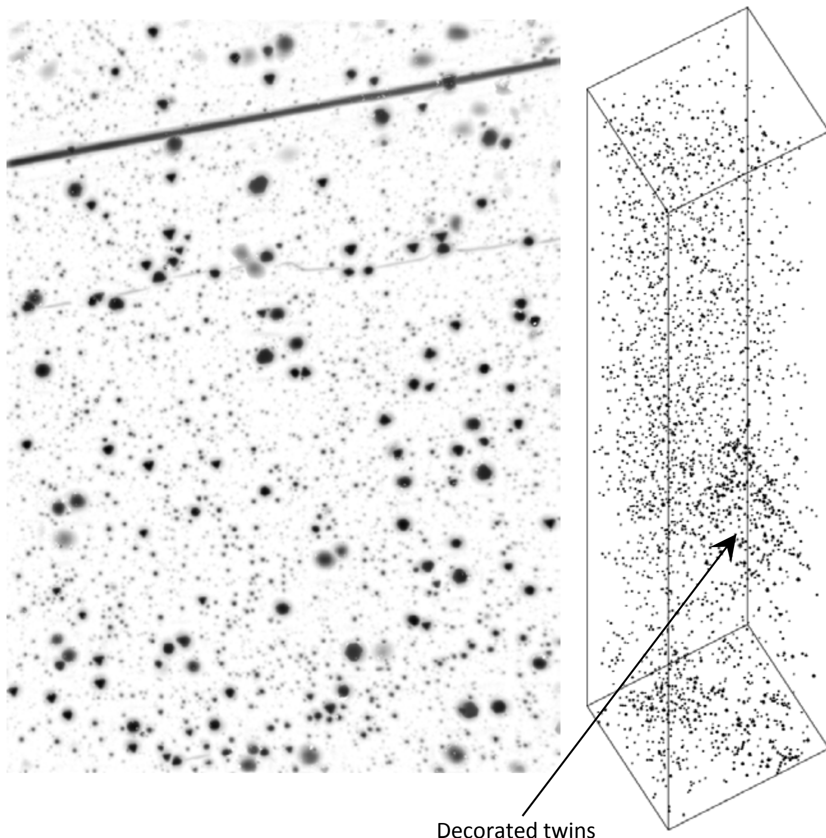
X-ray maps of the same areas of a 1mm thick CdZnTe device at different spatial resolutions

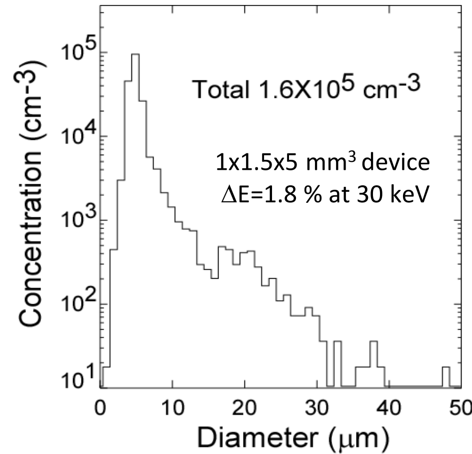
Carini et al., "*Effect of Te precipitates on the performance of CdZnTe (CZT) detectors,*" Appl. Phys. Lett., **88** (2006) 143515-1

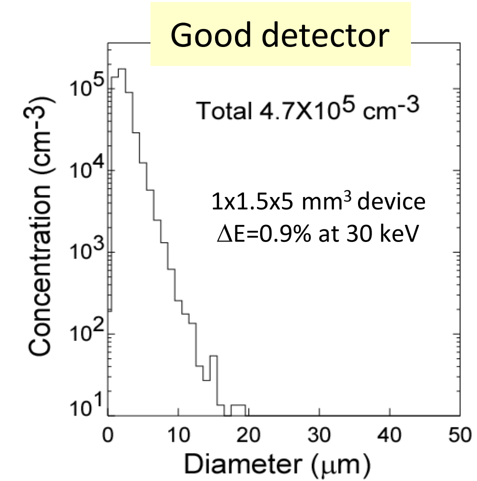
Defect/performance metrology – IR transmission microscopy

IR system allows "in-depth" images of Te inclusions, collapsed on a single plane from which it is possible to do a 3-D reconstruction of images. Can be used to measure sizes and inclusion concentration.

Example of the crystal with high concentration of Te inclusions. 1.1 x 1.5 x 10 mm^3







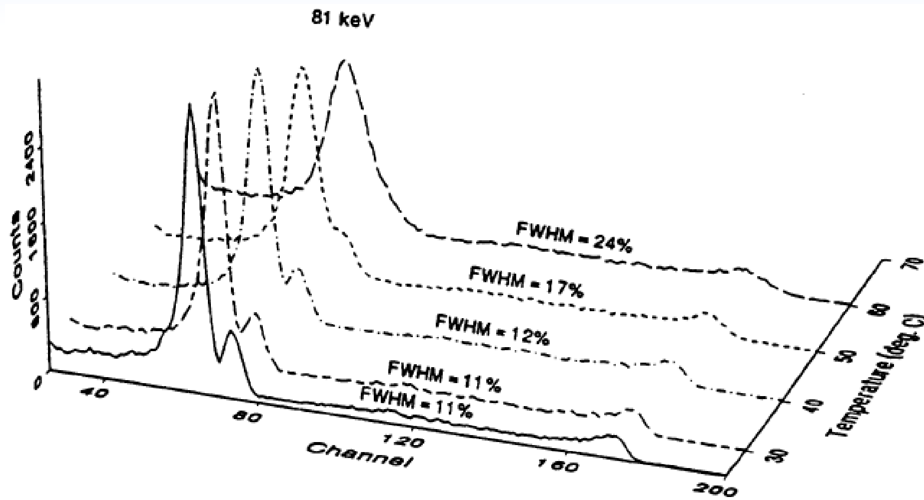
For each inclusion measure x,y,z, and diameter

Plug data into the model to generate X-ray response maps and pulse-height spectra

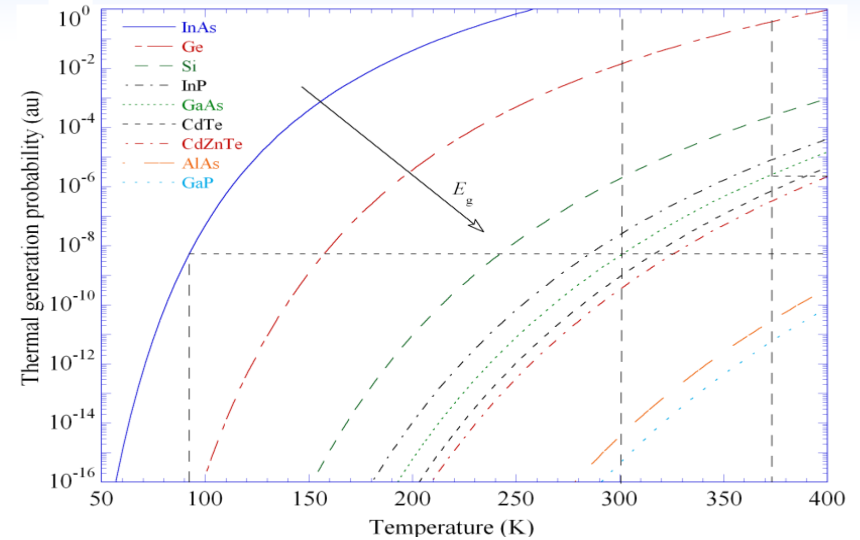
Currently, the model assumes that Te inclusions are opaque to carriers. It depends on a single adjustable parameter: the ratio between effective and actual size of inclusion

Bolotnikov et al., *Extended Defects in CdZnTe Radiation Detectors*, IEEE Trans Nucl. Sci, **56** (2009) 1775.

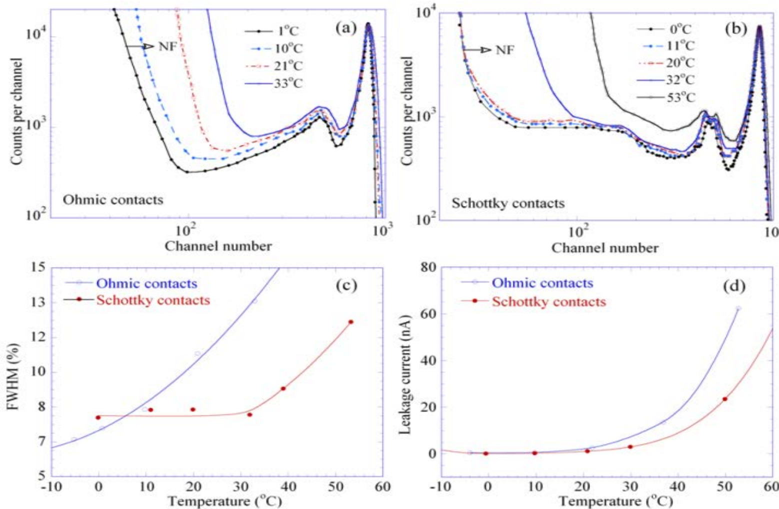
Performance limiting effects
3) Temperature degradation effects



The progressive degradation of spectroscopic performance of a CdZnTe detector with increasing temperature (from Egarievwe, et al., *SPIE*, **2305** (1994) 167).



The probability of thermal electron-hole pair generation as a function of temperatures



Effects also depend on contacting system

Temperature dependencies

(GaAs)

Intrinsic components $$P(T) \sim T^{\frac{3}{2}} \exp\left(-\frac{E_g}{2kT}\right) \qquad \mu_e \sim 8000\left(\frac{300}{T}\right)^{2.3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$$

External components – ohmic bulk leakage

$$I(T) \sim T^2 \exp\left(-\frac{E_g(T)}{2kT}\right)$$

with blocking contact leakage

$$I(T) = A^* T^2 \exp\left(-\frac{e\phi_b}{kT}\right)$$

External components – surface leakage

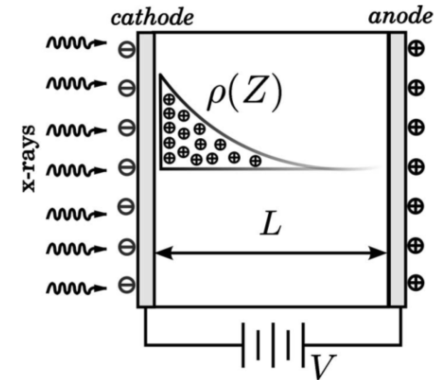
$$I(T) = cT^2 \exp\left(-\frac{\phi_b}{kT}\right)$$

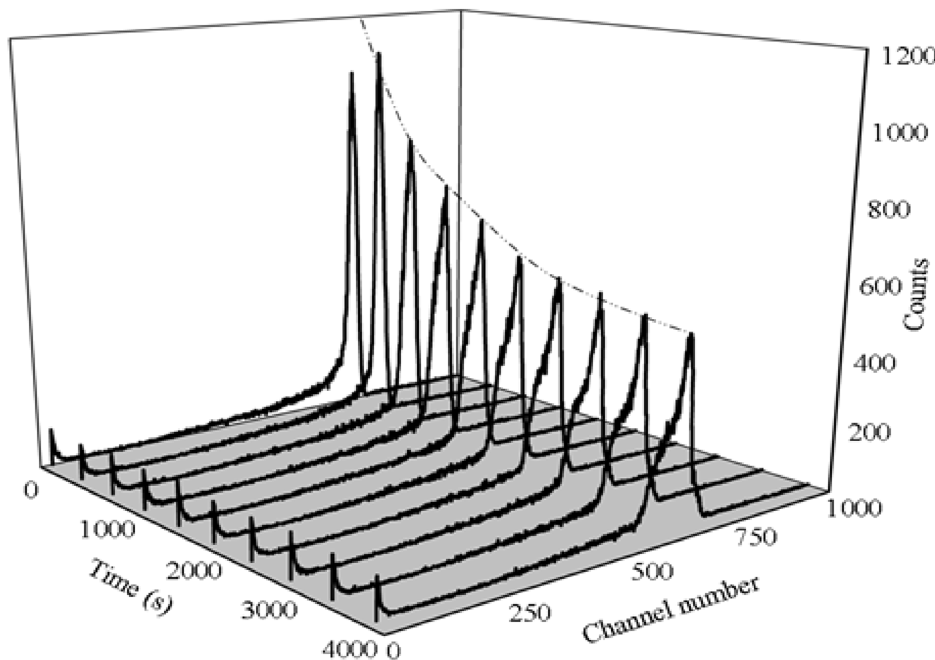
All strong dependencies

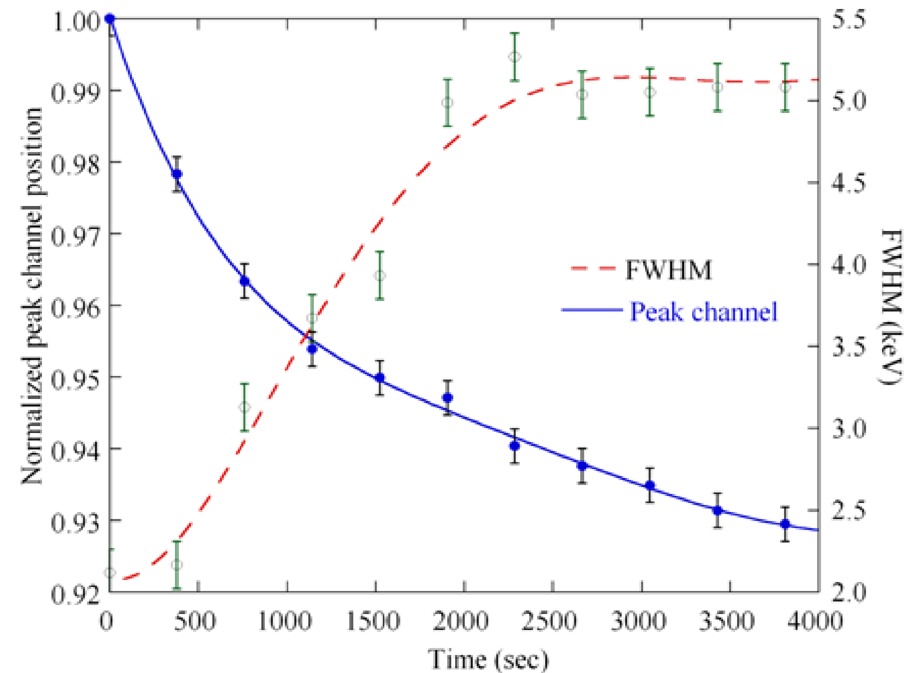
Performance limiting effects 4) Polarization

Time dependent build up of space charge due to mid-level traps (~0.8 eV) $\tau_{ionization} < \tau_{deionization}$

- bias induced - deep acceptor levels (depends on length of time bias applied, not on radiation level (examples, CdTe, HgI_2)
  - ionic conductivity (TlBr, AgCl)
- radiation induced - depends on radiation level and only relevant for high fluxes (examples include CdZnTe)





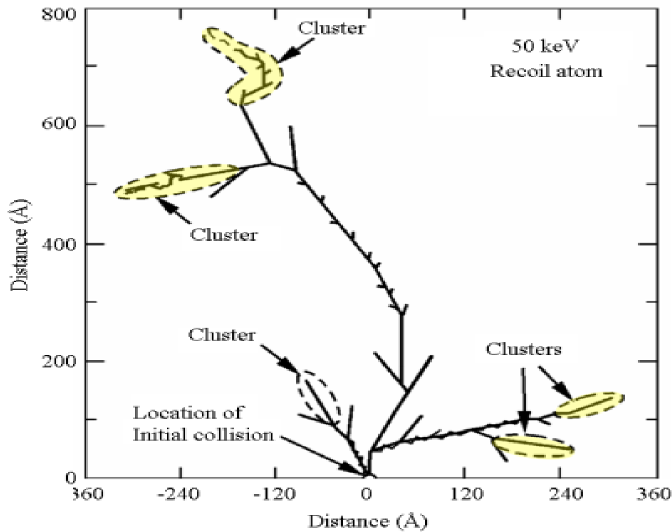


Polarization effects in a 5 × 5 × 2 mm^3 TlBr planar detector observed when exposed to a 50mm diameter 60 keV, 1 kHz, synchrotron beam

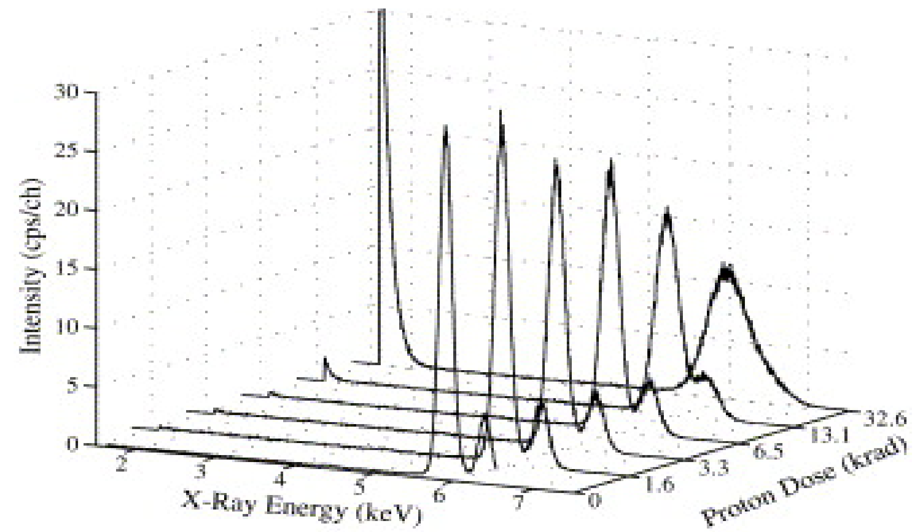
Performance limiting effects 5) Radiation effects

a) ionization, in which charged particles ionize the atoms in a device causing an instantaneous release of charge. In bulk materials this charge dissipates by either diffusion or drift in an electric field. However, in structured devices the build-up of localized charge can damage devices - particularly in the vicinity of an interface.

b) displacement, in which a device atoms are literally displaced and removed from their equilibrium positions introducing disorder into the crystal lattice structure. The consequences are the introduction of additional energy levels into the band gap which act as trapping and generation/ recombination centers, altering the semiconductors electronic properties.



Displacement damage in Si for the case where the energy transferred to the lattice site is more than 10^3 times greater than the displacement threshold energy The displaced atom can initiate a “cascade”, displacing many thousands of atoms.



X-ray spectra for the irradiated and non-annealed Si pin-detectors (shaping time 6 µs), after each proton exposure. A severe degradation in the energy resolution is already observed for proton doses of the order of 5–10 $krad_{(Si)}$(Si).

The factors affecting the calculated absorbed dose. For inter-comparison we list the absorbed doses for a proton irradiation of 2.66×10^9 p cm s^{-1}. The data are ranked by the product of the average nuclear charge and atomic density. The last column gives the “Tolerance” index for each of the materials , which does not track the absorbed dose.

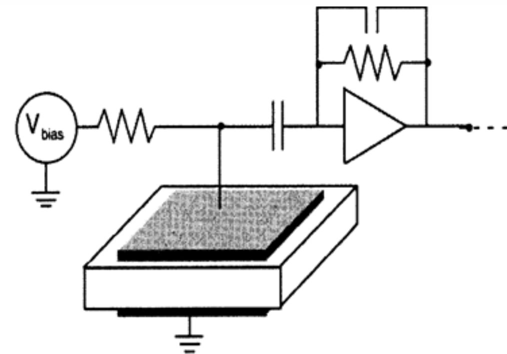
Compound	Bandgap eV	Atomic density cm^{-3}	Av. Nucl. Charge	Product cm^{-3}	Absorbed dose krads	Tolerance
CdZnTe	1.57	1.57×10^{22}	109.5	17.15×10^{23}	0.23	5
TlBr	2.68	1.60×10^{22}	53.2	8.52×10^{23}	0.60	3‡
HgI_2	2.13	0.84×10^{22}	92.1	7.81×10^{23}	1.05	1
GaAs	1.43	2.21×10^{22}	32.0	7.08×10^{23}	2.00	2
InP	1.35	1.98×10^{22}	27.1	5.38×10^{23}	1.31	4†
Si	1.12	4.97×10^{22}	5.29	2.63×10^{23}	2.00	6

‡moved from 2nd position to 3rd because of much increased polarization effects.

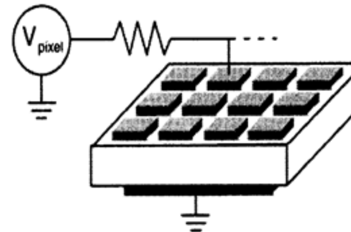
†moved to 4th because of its very poor initial energy resolution and its electronic and structural similarity to GaAs.

Improving performance - single carrier sensing

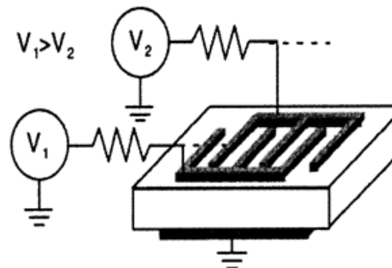
- Risetime discrimination
- Hemispherical geometries
- Frisch grid/ ring
- Small pixel effect
- Drift strip
- Ring drift
- Coplanar grid



Single element planar structure
(simple, thickness limited, ΔE heavily dependent on transport properties.)



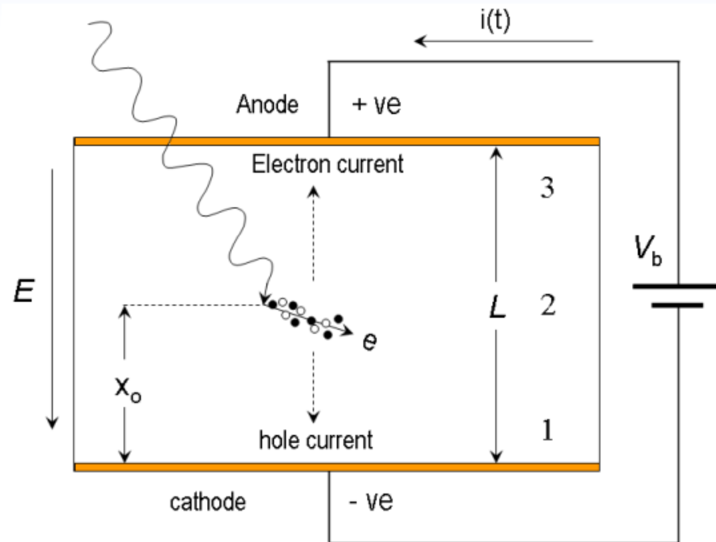
Pixel detector structure
Simple, small pixel effect – very good energy resolution, charge sharing complicated electronics/readout.



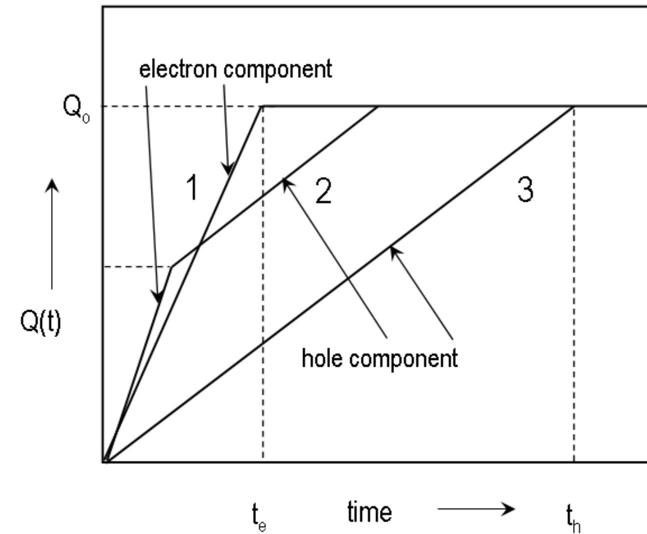
Co-planar grid structure
(good resolution, large volumes possible, complicated photolith.

However, we need a difference of ~ a factor of 10 in the mu-tau products to be effective

Risetime discrimination technique

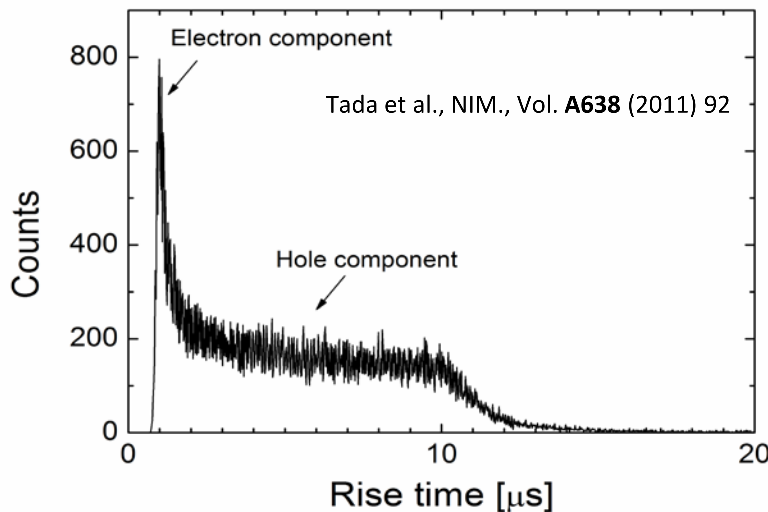


$$t_e = \frac{L}{\mu_e E} \qquad t_h = \frac{L}{\mu_h E}$$



$$i = \frac{dQ}{dt} = q\vec{v} \cdot \vec{E}_w$$

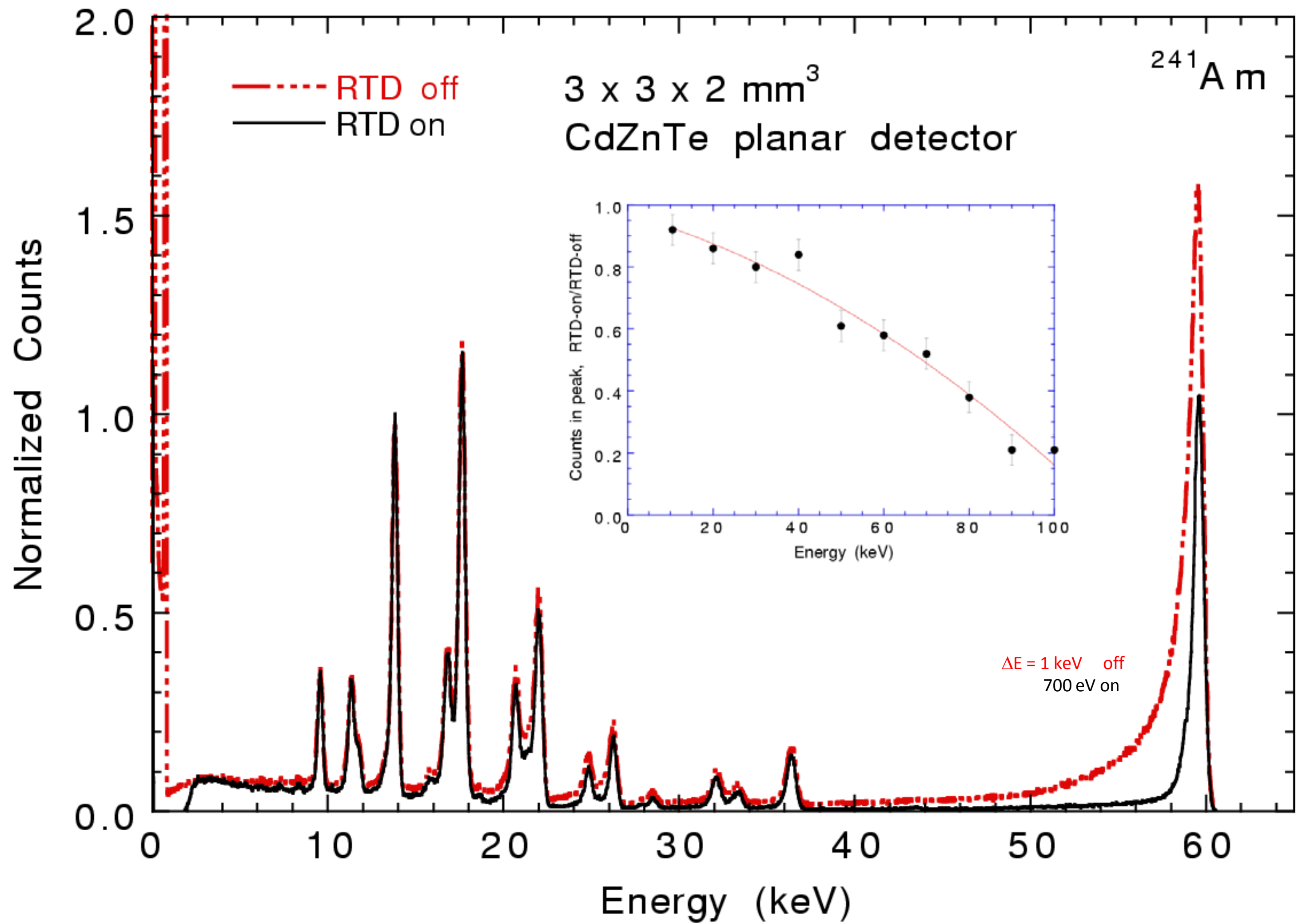
$$I_{eo} = Q_o\left(\frac{\mu_e E}{L}\right) \qquad I_{ho} = Q_o\left(\frac{\mu_h E}{L}\right)$$



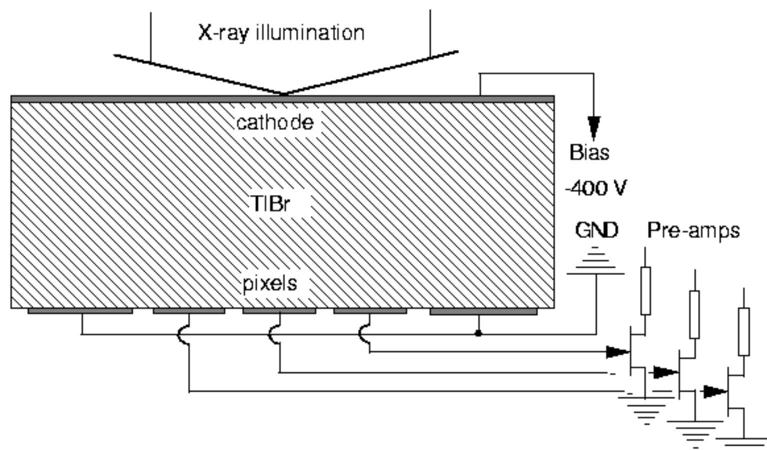
When $\mu_e >> \mu_h$ the current pulse induced by the electrons will have a much larger amplitude and shorter duration than that induced by the holes. For interactions in the bulk of the detector, the induced signal will be a composite of electron and hole components whose relative strengths will now depend on the depth of the interaction. In RTD methods, all pulses whose risetime exceeds a pre-set threshold are rejected - in fact, those events that would normally lie in the tail.

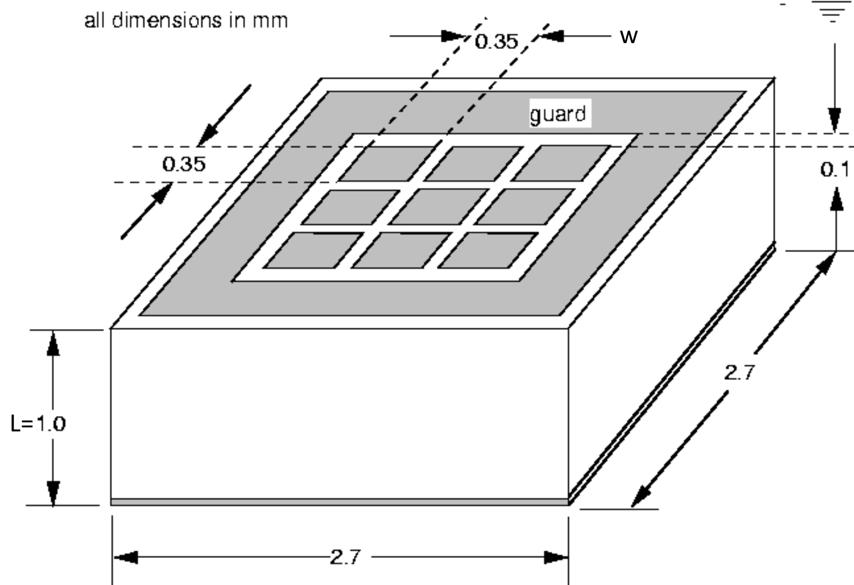
Jordanov, Nucl. Instr. and Meth., Vol. **A380** (1996) 353

Risetime discrimination 3 × 3 × 2 mm^3 CdZnTe detector

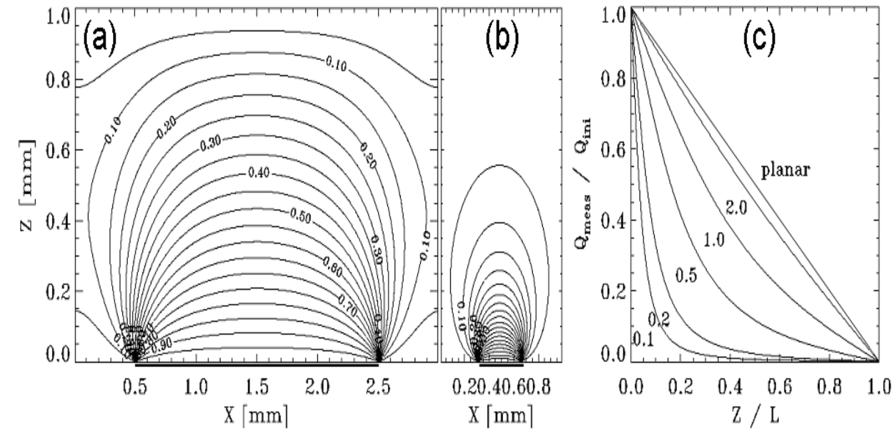


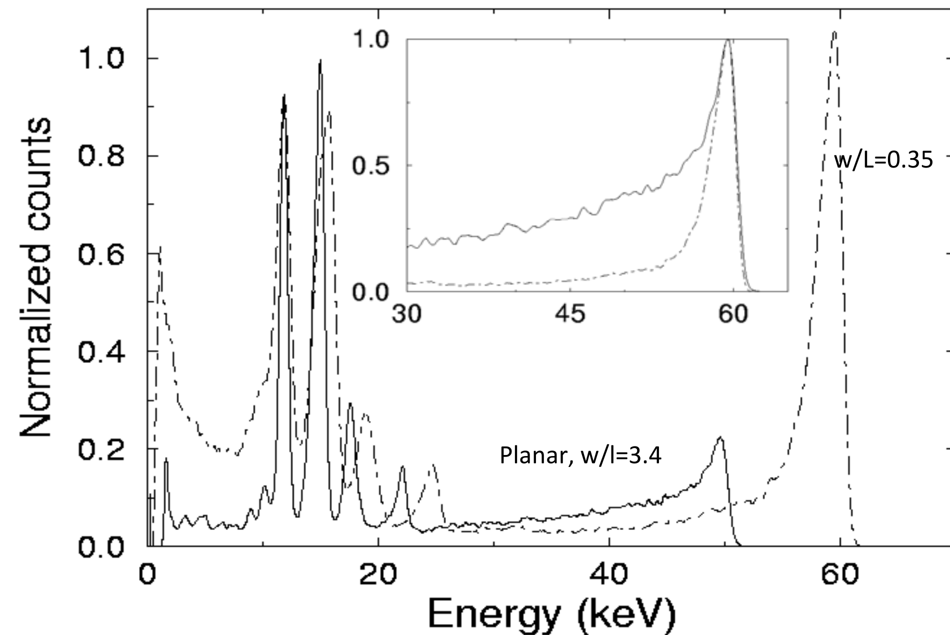
Small pixel - near field effect



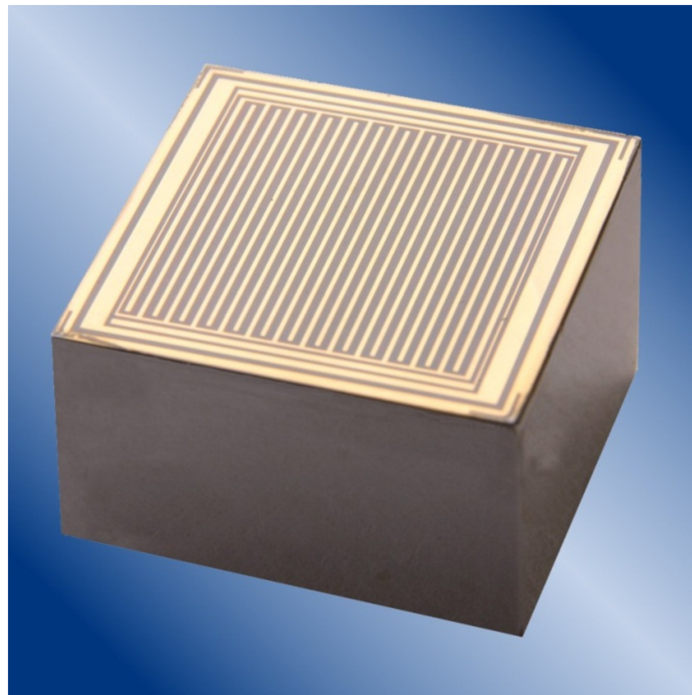


Weighting potential distributions

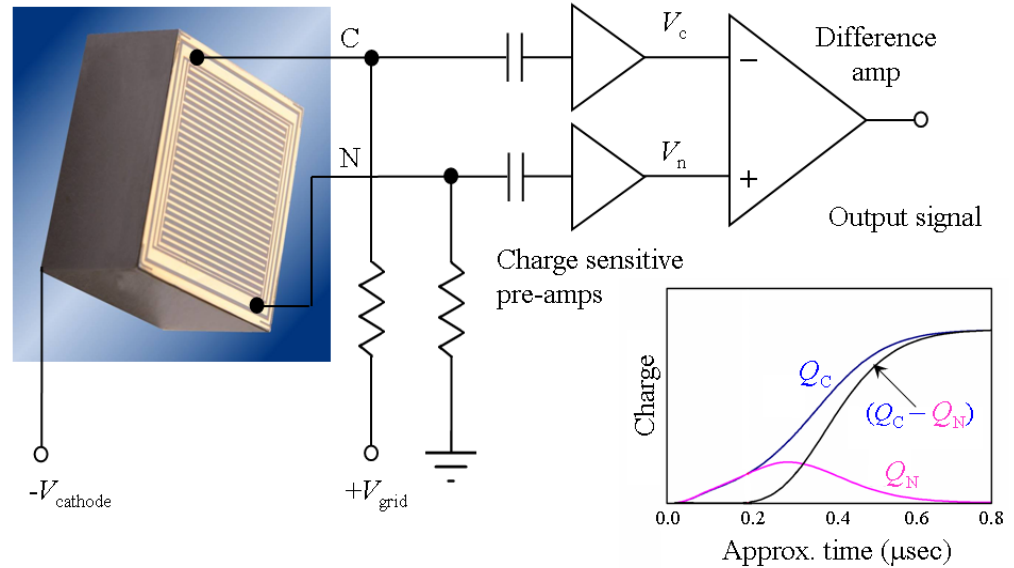


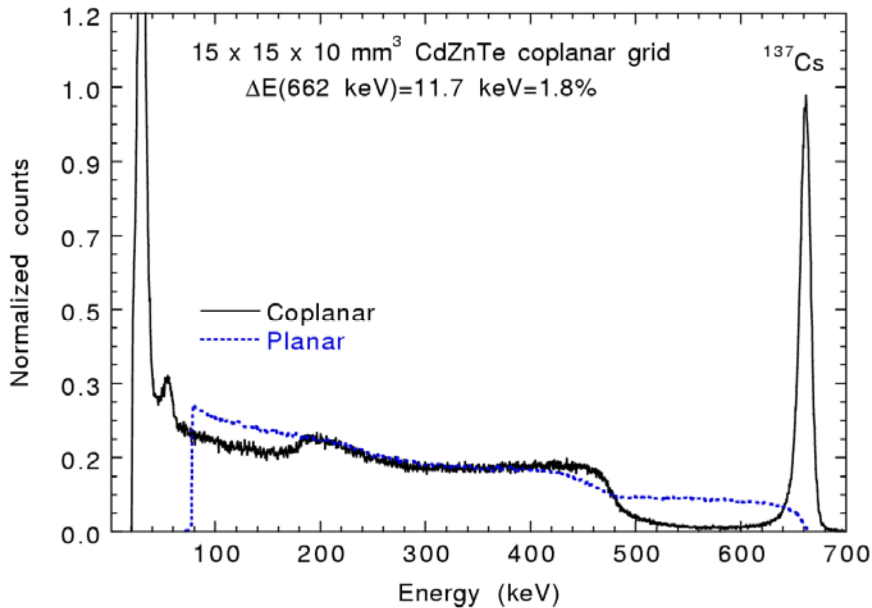


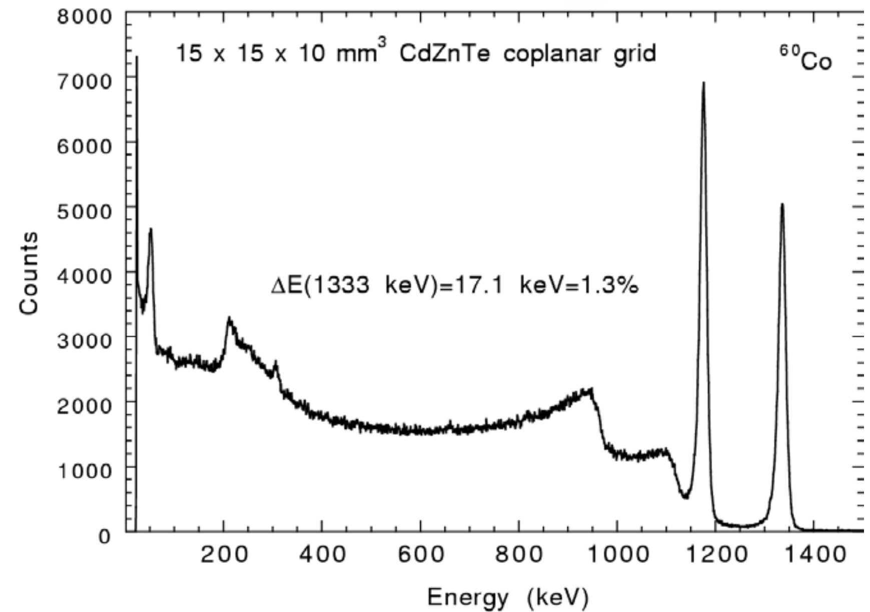
Coplanar grid technique



Luke, IEEE Trans. Nuc. Sci., Vol. **NS-42** (1995) pp. 207–213







A. Owens, Nucl. Instr. and Meth., Vol. **A563** (2006) 242

The wish list – towards the ideal conventional detector

Summary of desirable material parameters for the development of the next generation of semiconductor detectors, in the form of a list of the minimum material and/or preferred values. Because of the uncertainty in end applications and compatibility between requirements, some of the recommendations are by necessity subjective.

Parameter	Minimum or recommended value	Reason/Comments
Composition	Binary (or pseudo binary)	To minimize stoichiometry errors.
Structure	Cubic (close packed)	To optimize density.
Density	> 5 g cm^{-3}	To ensure good stopping power.
Growth technique	Epitaxial, FZ	Allows the possibility of integrated electronic structures.
Contact barrier height	< 0.4 eV	To ensure the contacts "look" Ohmic (i.e., with a resistivity $< 10^{-3}\Omega m^2$).
Effective atomic number, Z_{eff}	> 40	For high stopping power.
Resistivity	$> 10^9\ \Omega$ cm	To allow high biases to be applied.
Hardness	> 500 kgf mm^{-2} (Knoop scale)	Chosen to be high enough to allow the use of a range of mechanical processing and bonding technologies.
Bandgap	Indirect	To limit radiative recombination.
Bandgap energy	$1.4 < \varepsilon_g < 2.2$ eV	Lower limit for room temperature operation. Upper limit imposed by mobility losses due to polar lattice scattering.
Static dielectric constant, ε (0)	< 5	To ensure low capacitance.
Ionicity	< 0.3 (Phillips scale)	Ionicity should be low to prevent problems with ionic conductivity and polarization
Majority carrier trapping centre density	$< 5 \times 10^{12}$ cm^{-3}	To ensure good charge collection.
Impurity concentration	$< 10^{15}$ cm^{-3}	Can adversely affect resistivity, mobilities and effective mass.
Mobility electrons	> 500 cm^{2}V^{-1}s^{-1}	Charge induction considerations
Mobility holes	10 or 500 cm^{2}V^{-1}s^{-1}	Lower value if single carrier sensing is used, upper value if not.
Majority carrier lifetime	$> 20\mu$s	To ensure reasonably high mu-tau products
Electron mobility-lifetime ($\mu\tau_e$)	10^{-3} cm^{2}V^{-1}	Minimum value really depends on application, X-rays or γ-rays.
Hole mobility-lifetime ($\mu\tau_h$)	$< 10^{-4}$ or 10^{-3} cm^{2}V^{-1}	($\mu\tau_h$) should be < 0.1 ($\mu\tau_e$) if single carrier sensing is employed.
Majority carrier effective mass	0.1 m_o	To ensure high speed operation.

New directions in detection techniques

- Engineered materials – lattice hybridization
- Reduced dimensionality materials

  - Quantum heterostructures
  - Radiation detection with nanosemiconductors (1-D)
  - Radiation detection based on 2-D materials

- Other degrees of freedom

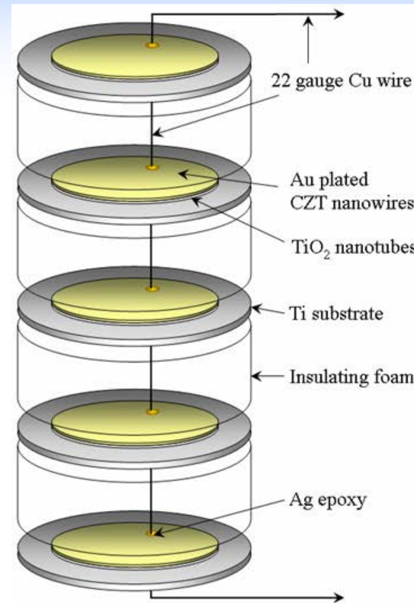
  - Radiation detection based on Spintronics
  - Radiation detection based on Valleytronics

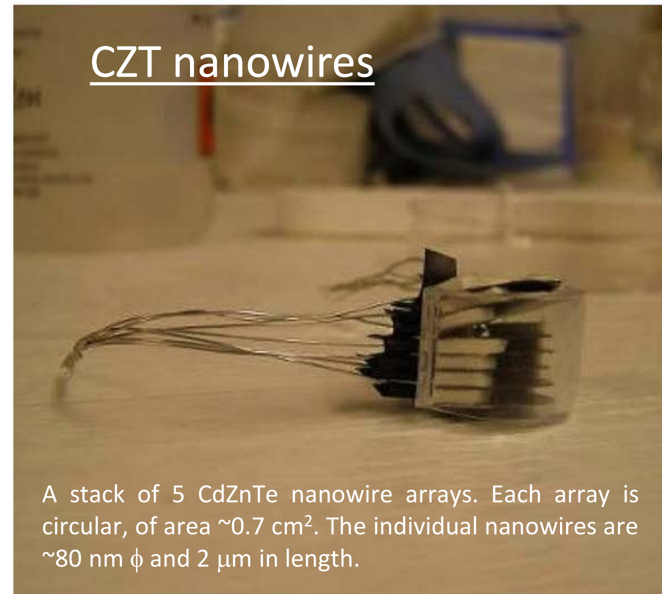
- Biological detection systems and intelligent photonics

Radiation detection with nano-semiconductors

Advantages

- Easy to manufacture
- Fabricate large detectors
- Can be grown by electrodeposition
- Better xtal perfection
- 1D conductors
- Biases can be low

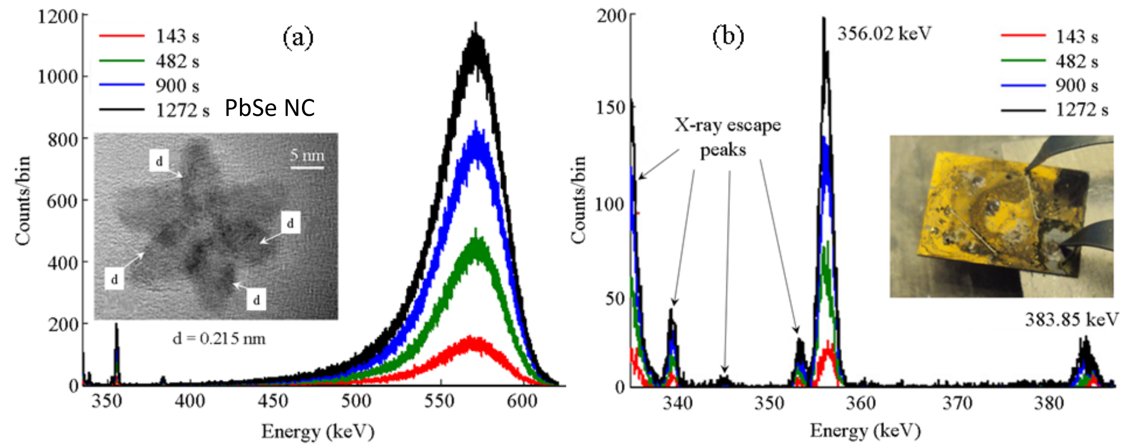




A stack of 5 CdZnTe nanowire arrays. Each array is circular, of area ~0.7 cm². The individual nanowires are ~80 nm ϕ and 2 μm in length.

PbSe nanocrystals

Detector 7 mmϕ x 5mm deep



ΔE at 662 keV same as HPGe

Energy-loss spectra measured from a ^{133}Ba and ^{241}Am source. The composite α-particle and γ-ray response is shown in (a) for a 1×1 cm thin (10's of μm) assembly of a conductive polymer and star-shaped PbSe nanoparticles. (b) An expansion of the ^{133}Ba γ-ray spectrum, in which the Pb and Se X-ray escape peaks are also apparent.

Gandhi et al., Proc. SPIE, Vol. **6959** (2008) 695904.

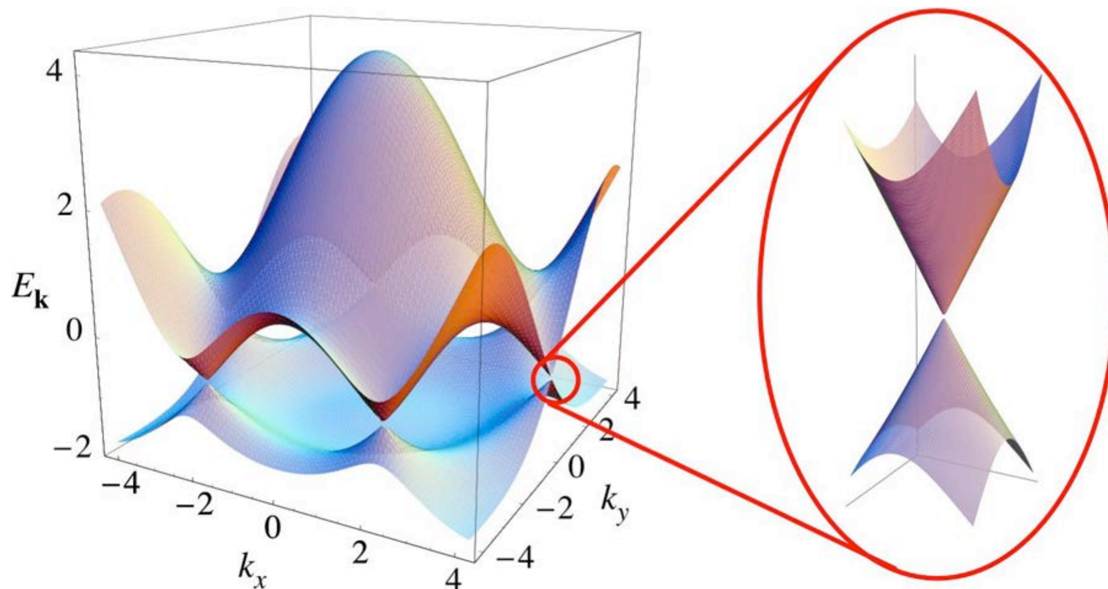
Radiation detection based on 2-D materials

For a 3D periodic crystal structure, the energy bands appear parabolic in *E*, ***k*** space near the conduction band minimum and valance band maximum and can be approximated by the well-known dispersion relationship

$$E(\mathrm{k}) = E_{\mathrm{o}} + \frac{\hbar^2 (\mathrm{k})^2}{2m}$$

Here we see that the allowed energies of the carriers are dependent on their effective masses. However, in the 2D structure of graphene, the energy bands near the conduction band minima and valence band maxima are conical and actually touch at six points in ***k*** space and the effective mass tends to zero – the so called K points. At these points, the dispersion relationship is given by

$$E(\mathrm{k}) = \pm\ \hbar v_{\mathrm{F}} \sqrt{k_{\mathrm{x}}^2 + k_{\mathrm{y}}^2}$$

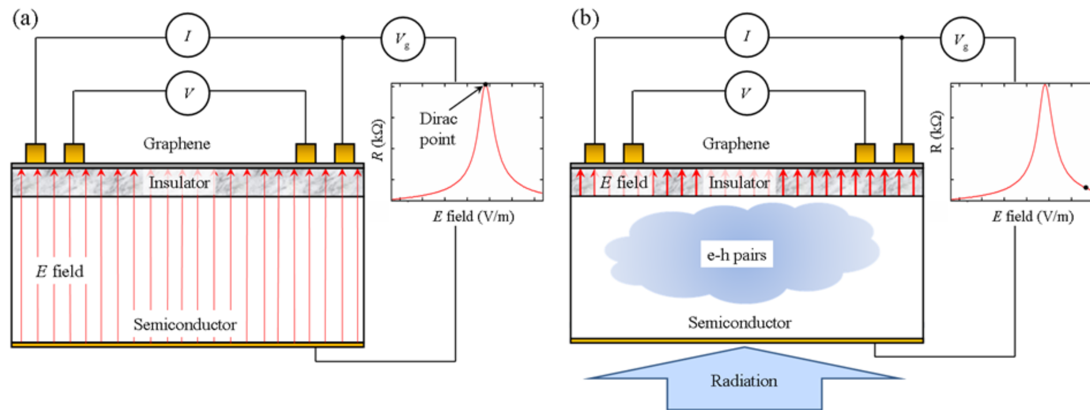


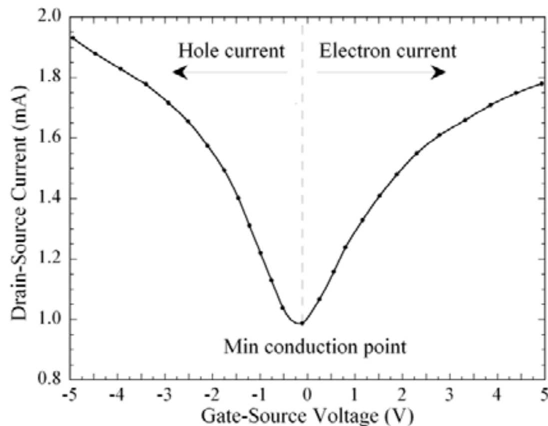
Which has no mass term. What this means is that while in standard semiconductors, the charge carriers can be described as electron waves obeying the Schrödinger effective-mass eqn., graphene electrons move according to the laws of relativistic quantum physics described by the mass-free Dirac eqn. Consequently, graphene has very high electron mobilities at room temperature, with values in excess of 15,000 $cm^2V^{-1}s^{-1}$.

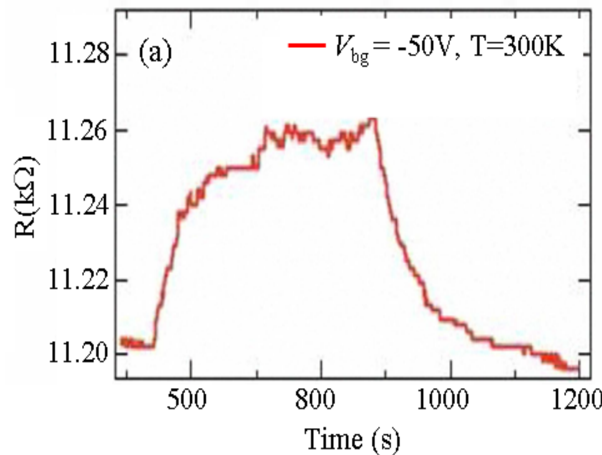
Castro et. al. *Rev. Mod. Phys.*,Vol. **81** (2009) pp. 109–162

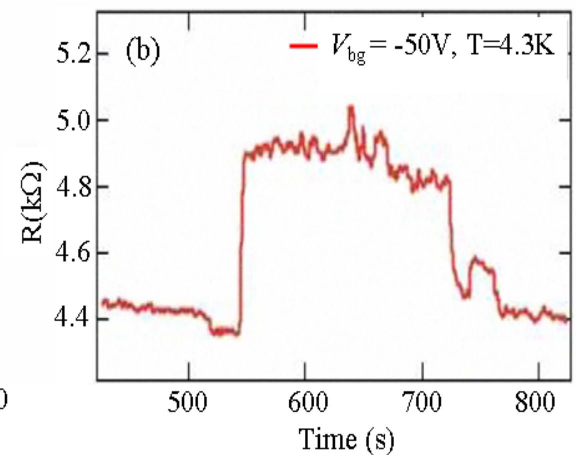
Radiation detection based on 2-D materials - graphene

A graphene FET (GFET) radiation detector - principle of operation. (a) A GFET consists of an absorber (undoped semiconductor), with an insulator buffer layer, which serves as a gate dielectric. V_g is the gate voltage applied to the sample. Current is supplied across the graphene sample, and the resistance of the graphene layer determined. In (b), incoming radiation produces ionization within the (intrinsic) semiconductor to create a conducting absorber. The gate voltage now only drops across the insulator. This results in an increased electric field, which is sensed by the graphene and its resistance changes as a result of the change in electric field as shown by the insets in the figure.









Left. GFET operation showing the variation of the drain-source current with gate source voltage using a thin p-type Si absorber. The curve reflects the Dirac curve and the device can be biased to collect either electrons or holes. (a) and (b). In (a) we show the response of a SiC based GFET to γ-rays and in (b), the response of a GaAs based GFET to X-rays. The initial rise in response corresponds to the point in time when a source is applied and the fall in response to when the radiation source is removed.

A. Patil et al., "Graphene Field Effect Transistor as Radiation Sensor", *IEEE Nucl. Sci. Symp*. Conf. Rec., (2011) 455.

Radiation detection based on new degrees of freedom

Tenent

Conventional detection systems only utilize the electrons charge

"The incremental advances in the current semiconductor nuclear detector technology will not be sufficient for developing the next generation of ultra sensitive, cost-effective detectors"

"Such developments will require the utilization of entirely new and transformative approaches"

Gary et al., IEEE Trans Nucl. Sci. conf. record, Vol. (2012) 4152-4155.

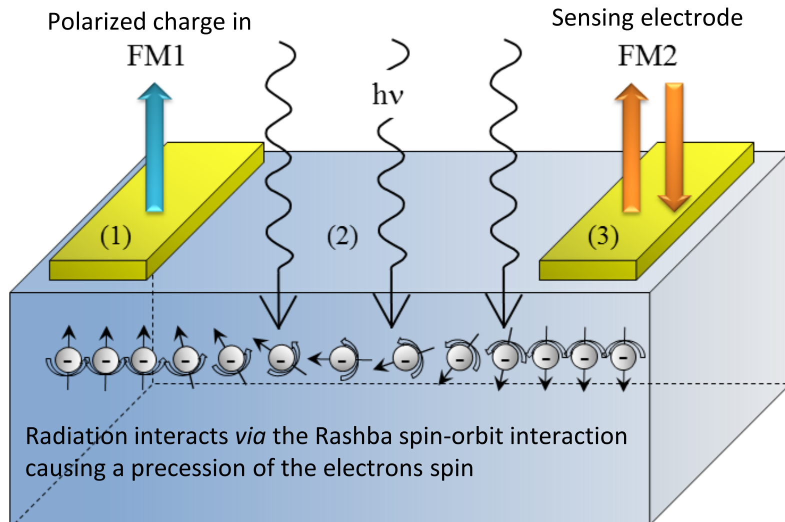
New degrees of freedom

Conventional detection systems only utilize the electrons charge

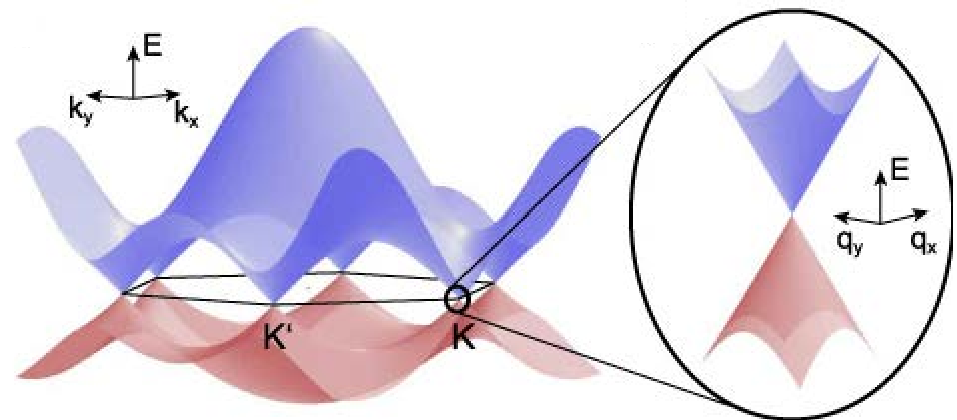
Use the more obscure internal degrees of freedom of the electron, for nonvolatile information processing

Spintronics[1]

The idea is to fabricate device that operates using not just an electron's charge, but also its spin and associated magnetic moment. In an electron, spin behaves like angular momentum, but is not related to any real rotational motion. As a result, the spin of an electron can be switched much more quickly than charge can be moved round. Charge can also be collected in the usual way by applying a potential across the device. . Spin is injected from a polarized source (such as a ferromagnetic metal (*e.g.*, Ni or Fe), FMl) into the active semiconductor region. The polarised electrons then interact with the incident radiation changing the spin of the electrons. The new polarization of the electron is then sensed at the other end of the semiconductor by a second ferromagnetic electrode (FM2)



FM is a ferromagnetic metal such as Ni or Fe



Valleytronics

Like spintronics, valley-based electronics, or valleytronics is another recent development that makes use of the more obscure internal degrees of freedom of the electron, for nonvolatile information processing. It relies on the fact that the conduction bands of some materials have two or more minima at equal energies but at different positions in momentum space. By controlling the number of electrons that occupy a particular valley, it is possible induce a valley “polarization”, which can then be used to transmit/process information. This new degree of freedom behaves mathematically in a similar way to the electron spin in that it acts like additional intrinsic angular momentum of the electron. Electrons can be valley polarized by scattering off a line of defects.

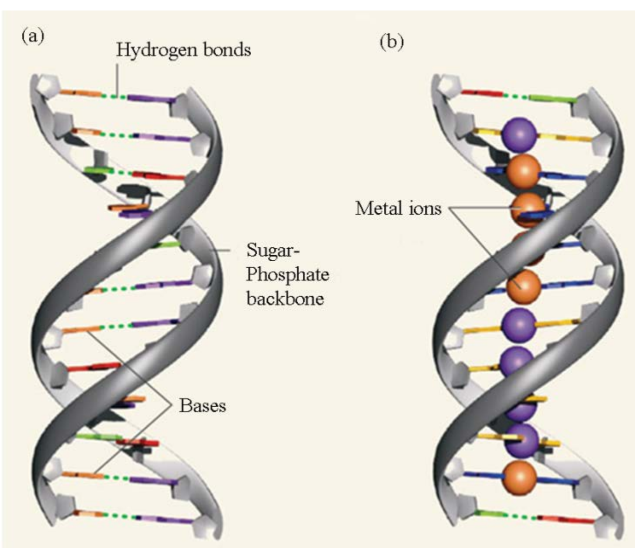
[1]a contraction of “spin transport electronics”

Biological detection systems and intelligent photonics

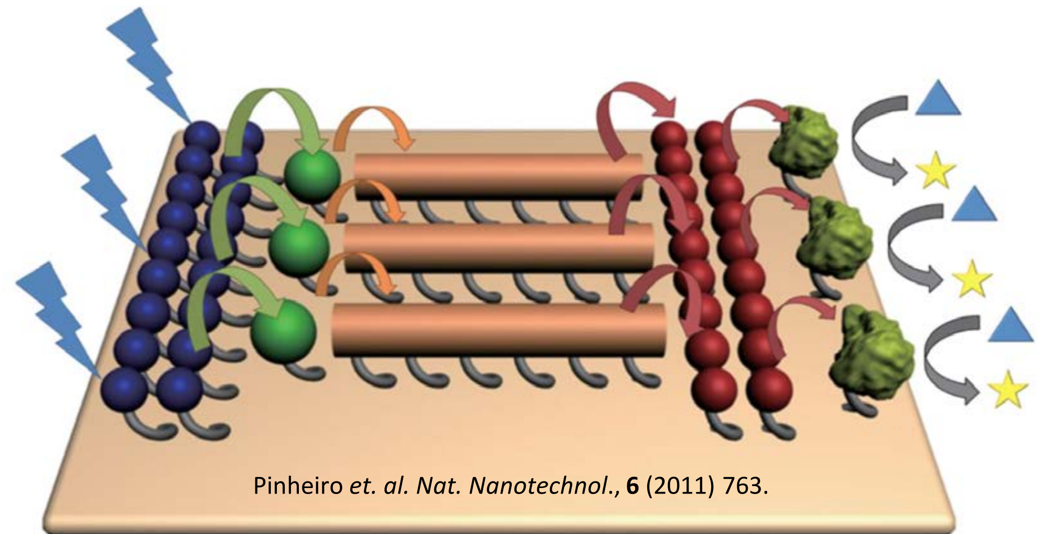
Several recent advances in nano-technology have demonstrated the viability of bio-metallic and bio-semiconductor interfacing, leading to the possibility that future detection systems may be directly interfaced to biological systems (the operator), or alternately, biological systems may be nano-engineered to be detection systems.

* porosity in III-V compounds, particularly, GaAs, GaP and InP leads to the possibility of animal cell:semiconductor interfacing as in the case of nanostructured Si (Bayliss, et al., "The Culture of Mammalian Cells on Nanostructured Silicon", *Advanced Materials*, Vol. **11**, Issue 4 (1999) pp. 318

* The porous semiconductor serves as both the adhesion substrate for Neurons which act as transducers/receivers. Preliminary work has demonstrated that mammalian cells can be cultured on nanostructured Si that remain viable over time - both in terms of respiration and membrane integrity.



(a) Single strands of DNA consist of a sugar–phosphate backbone decorated with organic bases. A double helix forms when the bases of one strand form hydrogen bonds to complementary bases on another strand. (b), Tanaka *et al.*, *Nature Nanotech*., **1** (2006) 190, have replaced bases in natural DNA with artificial ones that bind specifically to copper ions (Cu^{2+}, purple spheres) or mercury ions (Hg^{2+}, orange spheres)



Schematic of a DNA-based machine for energy transfer and photonics. The blue, green and red spheres and orange rods represent photonic components that can serve as light-harvesting and energy-transfer materials. The uneven green spheres represent enzyme or membrane complexes that can be used as final energy or electron acceptors. These act as molecular transducer units, where light is transformed into chemical potential, represented by the transformation of substrate (triangles) or into a higher-energy product (stars).

Matczyszy, Olesiak-Banska "DNA as scaffolding for nano-photonic structures", *J. Nanophotonics*,.**6** (2012) 064505

esa

Conclusion

We need better material and to explore other degrees of freedom – until then targeted material engineering (e.g., dimensional reduction) and use single sensing techniques

for more information see