Cs_3Sb and Ag-O-Cs as Diode Detectors for Low Energy Photon and Particle Detection:

Time Resolution, High Rates, Radiation Resistant

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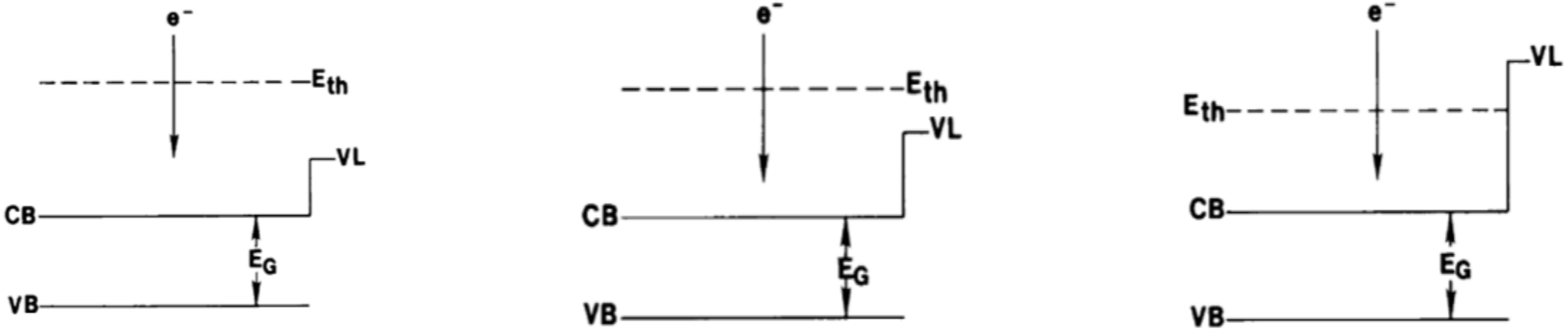
Physics Cases:

- Signals of energy, time, rate and position via signals from energy deposits from photons, neutrinos and charged and neutral massive particles are required for discoveries and measurements in low through high energies.
- Better S/N, very low energy detection thresholds, Timing Precision, High Rates and Radiation Resistance are of interest.
- The energy deposited by possible interacting dark matter particle candidates in a detector suggested here may be as low as or lower than ~10’s of eV.

Jiffy Diode Ion Detectors:

- Lowest known bandgaps: E_g operation must be cooled to LHe or lower to avoid thermal noise generation.
- Probability per unit time for e-hole pairs thermally generated $P(T) = CT^{3/2} e^{-Eg/2kT}$, Eg is the band gap energy, k is the Boltzmann constant and C is a proportionality constant characteristic of the material.
- Operation at 300°K: Rule of Thumb: Eg > ~1.3 eV so that thermally generated carriers do not dominate detection of low energy events.
- Example: Si (Egap ~ 1.1 eV) often needs cooling; SiPM often require cooling to

  -30C° for sufficiently low noise single p.e.(Photoelectron) detection.
- Epair: Ep=Eg +Ea (Ea=electron affinity) $=E_{threshold}$ similar to/related to work function ϕ but can be more or less than the vacuum level VL.
- Semiconductor energy bands are divided into 3 generic classes. The levels are relative $-E_{th}$(Ep), the valence band VB and the conduction band CB are all shown as equal energies in the 3 classes, in the same proportions or ΔE to each other (not always the case)



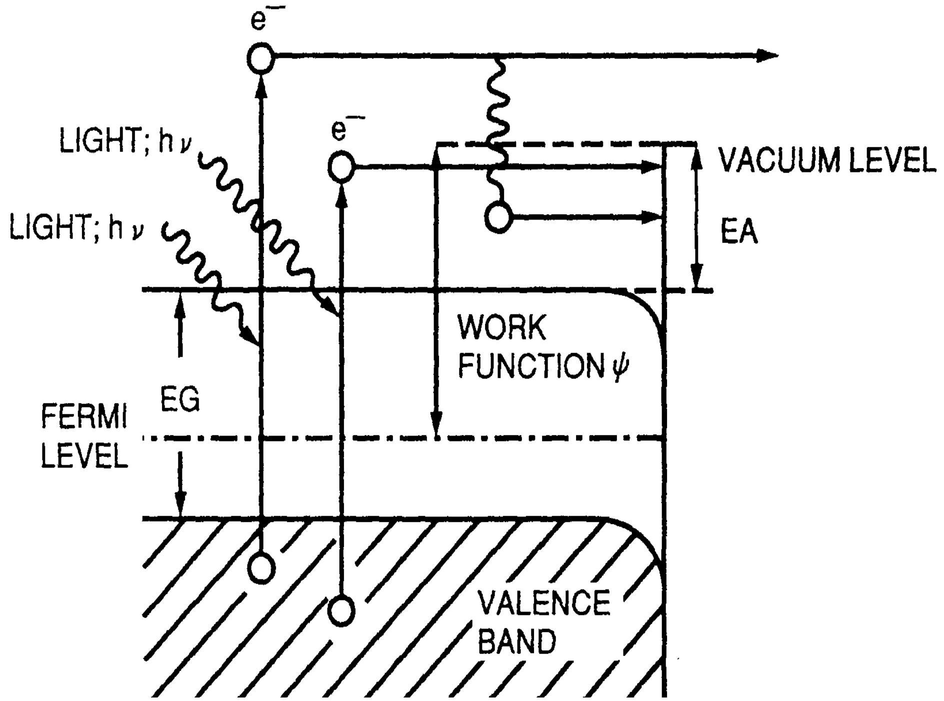
Left and Middle: semiconductors where the threshold energy for pair production is above the vacuum level VL.

- When e-hole pairs are produced, the electron has a chance to escape, as its energy can be above the vacuum level, and can be a photoelectron (p.e.) or photoconducted electron.

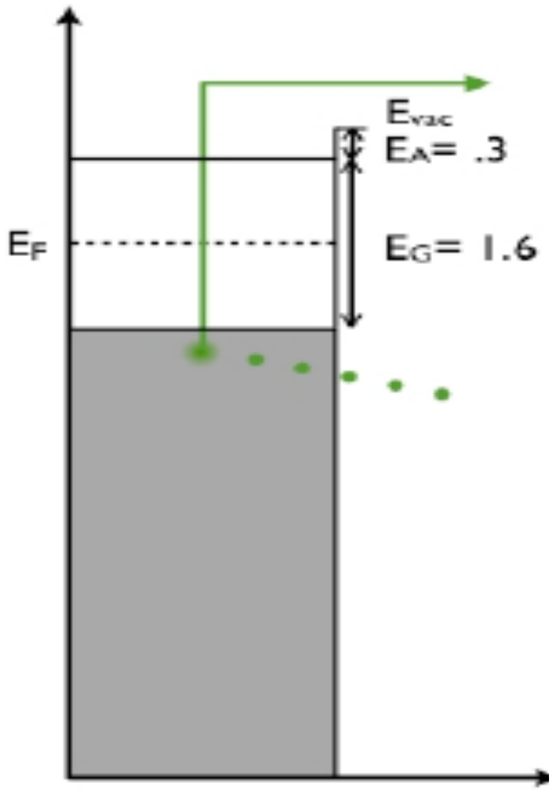
- Left: best semiconductors for photoemission: energy levels qualitatively similar to the left figure; once a pair is made, over a large range of energy depositions, the electron can escape
- Middle: photoemitters with a restricted range of emissions.
- Right: Poor photoemitters - like Si or Ge - where most of the electron-hole pairs do not have enough energy to be above the vacuum level (work function) to escape. However, the electron-hole pairs are above the conduction band and can be drifted to electrodes or a junction.

- Multi-alkali and GaAs photocathodes are like the left most diagram, while most mono-alkali PC are like the middle diagram.

- Alkali photocathodes typically the work-function/E_{thresh} is slightly more than Eg+Ea.

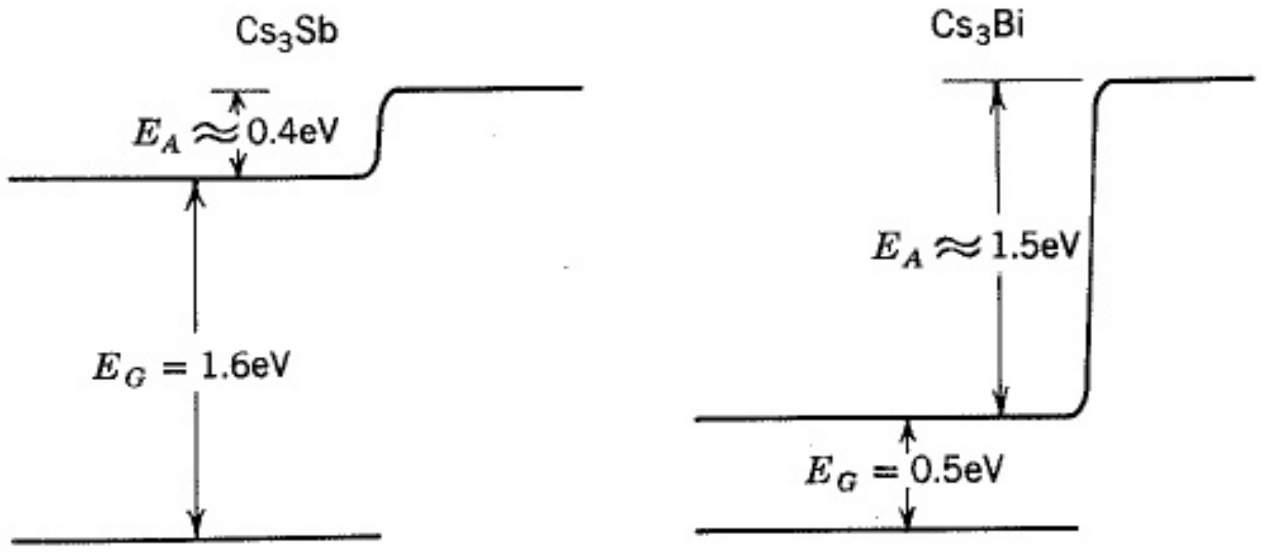


Generic Photoemitter



Cs_3Sb (S-11) Cs_3Sb

The Cs_3Sb semi-conductor energy level band diagram –
the energy for pair production E_P ~ Ea+Eg= 1.9-2.0 eV,
near the vacuum level and like the 2nd class Band Diagram



• Cs_3Sb and Cs_3Bi: equal pair energies Ep ~Ea+Eg ~2 eV, *but very different Eg*. *Si is analogous to* Cs_3Bi, with a low Eg so that thermal carriers more easily generated and a source of detector noise. Cs_3Sb Eg suppresses thermal carriers/noise relative to Si*, but has a lower Epair*.

• Cs_3Sb: Eg inhibits 300°K thermal energy from promoting carriers above the Fermi level – operate with minimal or no cooling for detecting many types of low energy events, which could include very low energy neutrino scatterings.

• Ex: *Si has a similar Ea/Eg >1 as has* Cs_3Bi *– Si has a low Eg = 1.1 eV and therefore requires cooling for many applications such as SiPM- or Si-like diode detectors compared, with* Cs_3Sb *with 1.6 eV Eg*. However, Si has an Ep=3.6 eV compared with Cs_3Sb Ep=2 eV – so Cs_3Sb can operate at room temperature with more signal than Si.

- *Energy Resolution* limit $\sigma \sim \sqrt{(F/n)}$, where the number of carriers $n \sim E/E_p$;

- F: Fano factor (~0.1 for semiconductor detectors - Ge~0.06).

- A basic figure of merit M for a detector material and E <500 KeV: $M \sim \rho Z^{3.5}/\sigma$. For higher energy, radiation length L_{rad}^{-1} which scales as a lower power of Z ie $\sim Z^2$.

- Semiconductor diodes or drift cells for calorimetry (Ge, CdTe, Si …)
    - Ge: superior semiconductor detector: resolution of ~0.2% at 662 KeV; peak/Compton ratios of 30 or even higher;
    - Ge: Eg = 0.7 eV, Ep = 2.96 eV; *but too large for extending present Dark matter searches*.
    - Si: pair energy Ep=3.6 eV is similarly too large, as is GaAs.

- Semiconductor materials normally used for vacuum photocathodes have much lower Ep.

- Cs_3Sb (S-11 photocathode-) : Ep ~ 2 eV pair energy.

- Cs-Ag-O (S-1) Commercial: averaged pair energy/work function Ep=0.7 eV in commercial applications

- Cs-Ag-O Small Patches ~few mm^2 as fabricated in research studies that the pair energy - a remarkable Ep = 0.4 eV

S.Asao, Proc. Math Phy – Math Soc. Japan 22, 448(1940); A. Lallemand and M.Duchesnes, Z. angew. Math Phys. 1, 195 (1950)

	Z	ρ(g/cc)	Egap(eV)	E_{pair}	μ_e, μ_{hole} $cm^2/V/s$	Lrad(cm)
Ge	32	5.3	0.7	2.98	≤3900, ≤1900	2.3
Si	14	2.3	1.1	3.6	≤1400, ≤450	9.4
GaAs	31,33	5.3	1.4	4.4	≤8500, ≤400	2.3
Cs_3Sb	55,51	4.6	1.6	2.0	10,000-10^6	1.9
Ag-O-Cs	55,47,8	7.1	<0.3	0.4-0.7	Predicted ~5,000	1.8-2.0

- In vacuum photocathodes the photoelectron escape depth is ~100's of atoms thick..
- A biased diode junction device does not have a restriction in thickness with an applied field.
- With metal electrodes a Schottky diode results with p-type Cs_3Sb or Cs-Ag-O
- ~10 nm thick defect, low-doped, or excess Cs layer forms an n-p junction.

1. Cesium antimonide (Cs_3Sb) - weakly bound cubic semiconductor,

- lattice constant 9.15 Angstroms, normally p-type from Sb excess displacement defects

- Very low electron affinity of 0.4-0.5 eV

- 300K° intrinsic resistivity ~1,000 Ω-m, ~ 10^{7-8} times higher than Sb/500 Ω-m of Ge at 77K

- mobility μ > 10^4 cm^2/Vs. (on defect filled films of thermal diffusion fabricated photocathodes - exceeding Indeed, on theoretical grounds, μ could exceed 10^6, like InSb) [].

- With precision assembly of films or tiles, displacement defects may be minimized, and may become more intrinsic rather than p-type.

- Polarizing of the material due to differing electron and hole mobilities, together with the overall high mobility, imply that very high rates of ionizing events may be sustained, exceeding 300 MHz, and ~10 ps timing is feasible.

J.J.Scheer and P.Zalm, Philips.Res. Rept 14, 584 (1959)
Sommer, A., "Photoemissive Materials" sections 6.5-6.8 [1968] J.Wiley
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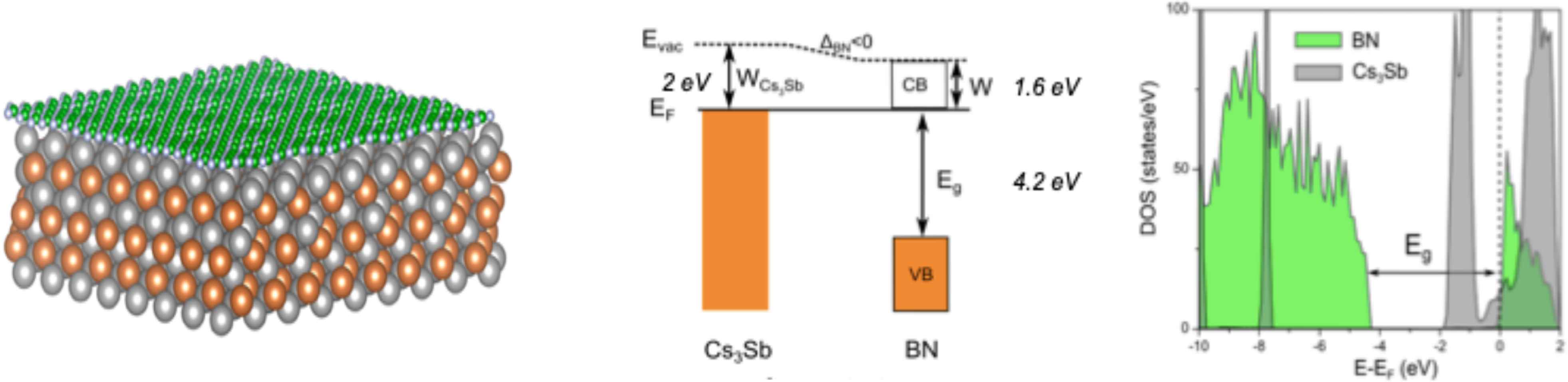
Wang , Pandey, Moody, Yang, Batista, J. Phys. Chem. C 121, 8399-8408 (2017)
Pavlenko, Liu, Hoffbauer, Moody, and Batista, AIP Adv. **6**, 115008(2016)
J.C. Sprenger et al, Electron-Enhanced Atomic Layer Deposition of Boron Nitride Thin Films at Room Temperature and 100°C, J.Phys. Chem. C 122(17), 9455-9464 (2018)

- Recently it has been shown that one molecular thickness of boron carbide (BN) or one layer of graphene can protect Cs_3Sb from air, important for practical detectors with minimal effects from air.
- Remarkably, the BN layer *lowers* the pair energy from 2 eV to 1.6 eV [], [] whereas graphene layers raise the pair energy to 2.1 eV[].



(L): Molecular model of layered Cs_3Sb with a BN (boron nitride; graphene similar) single molecular layer top-side covering. The e-hole pairs could be drifted parallel to the atomic planes in perfect crystals that result from (near)atomic layer assembly. ***(M):*** Remarkably, the implied electrostatic potential *lowers* the work function of Cs_3Sb from 2 eV to 1.6 eV **(R)** Energy bands of Cs_3Sb+BN.

Wang, Yang, Moody and Batista, NPJ 2D Materials and Applications 2, 1-9 (2018)
Wang , Pandey, Moody, Yang, Batista, J. Phys. Chem. C 121, 8399-8408 (2017)
Pavlenko, Liu, Hoffbauer, Moody, and Batista, AIP Adv. **6**, 115008(2016)

BN and graphene atomic layers deposit at T<100°C [].

Cs_3Sb

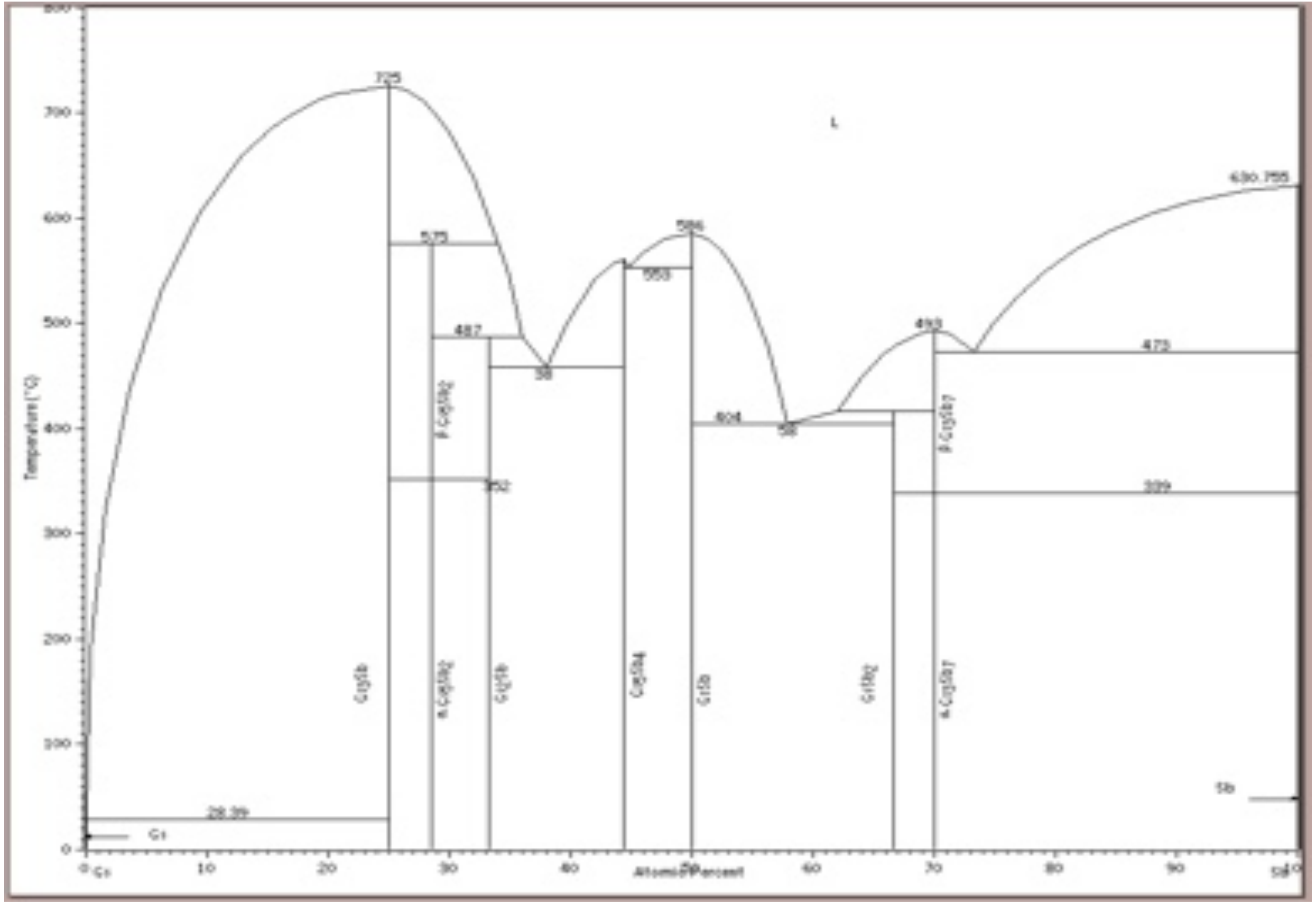
- Pair Energy: Ge 2.98 eV, Cs_3Sb 2 eV [], [], [] or 1.6 eV if coated with BN Cs_3Sb
- Cs_3Sb Intrinsic resolution: better than Ge by ~√(2.98/2) ~1.22 or √(2.98/1.6) ~1.36.
- Bandgap 1.6 eV, exceeding Si (1.1 eV), CdTe (1.47 eV) -> thermal noise minimal at room temperature.
- Thermal noise current 200°K ~between 10,000-20,000 times lower in Cs_3Sb than Silicon, which alone makes it interesting as a detector, *if defects and impurities are controlled*.
- Ep: 0.4 eV above Eg a potential breakthrough material unlike Si, Ge, …others.
- Density Cs_3Sb 4.6, compared to 5.3 for Ge
- Z: Cs_3Sb is 55, 51 (average ~54), compared with 32 for Ge.
- Photoelectric absorption ~4-5 times higher for Cs_3Sb compared with Ge at ~662KeV gamma-rays -> Peak/Compton ratio should exceed Ge.
- (Lrad Cs_3Sb)/(Lrad Si) = 9.4/1.9 = 4.9
- Because of its larger atomic number its photoelectric absorption is larger, its peak to Compton ratio is larger, and its radiation length is shorter. It has better resolution as pair energy is lower.
- It does not need to be cooled for applications at room temperature, because its bandgap is large, even larger than for Si.
- Compared to Ge, the cost of the highly purified raw material is negligible, albeit the fabrication costs are at present high.
- The speed of a Cs_3Sb detector could be 5-10x faster than Si (mobility is substantially larger, by factors of 7-700) with nearly equal e and hole mobility, making it able to take high rates without polarizing.

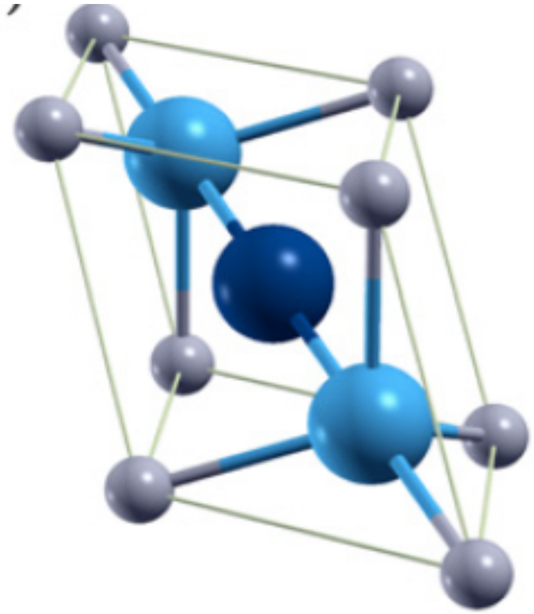
- Sommer, A., "Photoemissive Materials" page 94 [1968] J.Wiley
- L.Apker et al., J.Opt.Soc.Am. 43, 78 (1953)
- W.E.Spicer, J.Phys.Chem.Solids22, 365 (1961)

Cs_3Sb

- Cs_3Sb: like NaI, it must be protected from the atmosphere and can be formed in a melt almost identically to that of NaI or CsI fabs, which may be justified in few mm thicknesses.
- Crystals of Cs_3Sb have been grown readily by an inert atmosphere or vacuum thermal melt, heating Sb powder with Cs metal particles at 725°C and their bulk properties measured []
- We know of no studies of Cs_3Sb used as a dE/dx detector.
- The technology to grow crystals of CsI and NaI occur at similar forming temperatures and such commercial facilities could be readily adapted to Cesium Antimonide. Today we can obtain Cs and Sb with much higher purities than the earlier experiments, circa ~60 years ago.

- K.H.Jack and M.M.Wachtel, Proc.Roy.soc., A239, 46 (1957)





L: Phase diagram for Cs_3Sb melts – Temperature vs atom% of Sb - perfect 25% stochiometry forms at 725 °C(the left-most peak).

R: Cs_3Sb peroskovite– note expansion of Sb(grey) due to 3 Cs(blue).

- ***2. Ag-O-Cs*** - the basis for the S-1 photocathode.

- Not used today for vacuum photoelectron detectors – low p.e. Quantum Effy + Noisy
- Noise/Dark current 300°K 4-6 orders of magnitude greater than the best bi-alkali photocathodes and 3-4 orders of magnitude larger than the Cs_3Sb S-11.
- Ag-O-Cs has the lowest work-function or pair energy of any other material known, as low as 0.4 eV [], []. A few mm thick tile cooled to <1K° could be a superior Dark Matter Detector, capable of generating ~100 electrons for ~50 eV deposited.
- Deposition on Si may lower it further by band bending or by electrostatic potential induced by protecting it with an atomic layer of BN and by graphene on top of the BN.
- The structure of Ag_2O amenable to incorporation of Cs.
- Basic reaction forming an Ag-O-Cs cathode: $Ag_2O + 2\ Cs \rightarrow 2\ Ag + Cs_2O$.
- The silver atoms *remain in the lattice* and are essential for the energetics.

- A. Lallemand and M.Duchesnes, Z. angew. Math Phys. 1, 195 (1950)

- N.A. Sloboleva, Radio Eng. Electron. 4, 11, p204 (1959)

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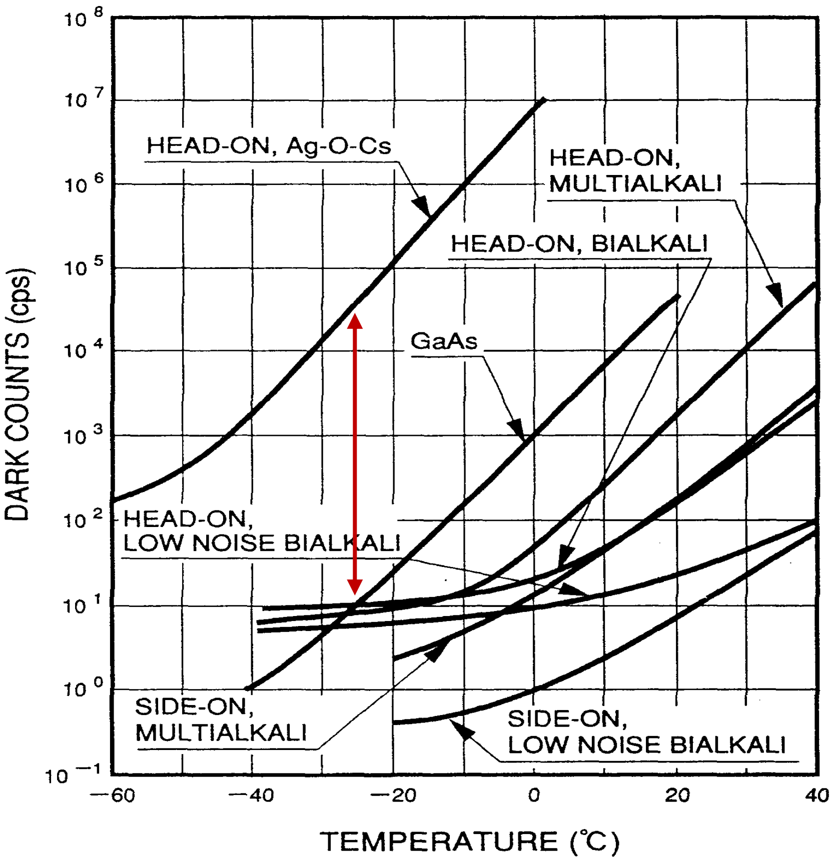

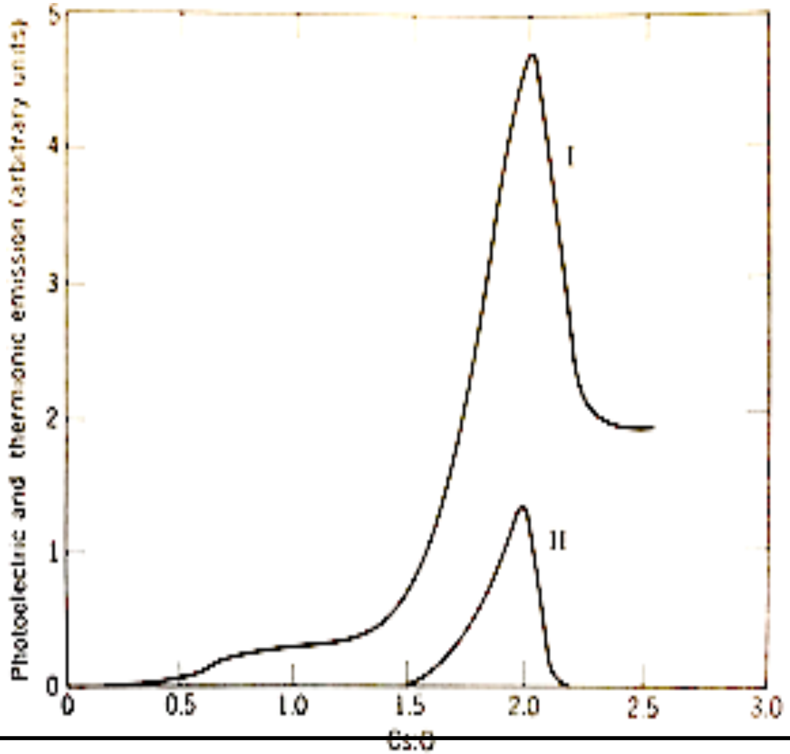

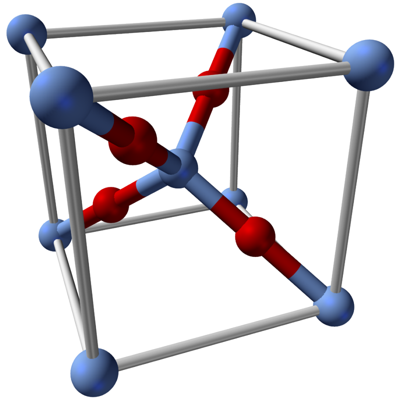

(L). Photocathode Dark Currents in PMT photocathodes [Hamamatsu] vs T. *The Ag-O-Cs dark rate is ~3-4 orders of magnitude larger than others from the very low energy needed to generate carriers.* ***Here it is a feature****…*

(M) (M) Electron emission (arb units) vs Cs:O fraction during reaction of silver oxide with Cs; photo (curve I) thermionic (curve II) [] – the material is optimized when the Cs:O ratio is 2.0.

(R)) The structure of Ag_2O is amenable to atomic layer assembly; incorporating atoms of Cs - despite a large atomic radius - can be added to form the Ag-O-Cs semiconductor

Hamamatsu PMT Handbook, Chapter 13, section 13.1

Y. Sayama, J.Phys.Soc.Japan 1, 13 (1946)