High Resolution optical spectroscopy in isotopically-pure Si using radioactive isotopes: towards a re-evaluation of deep centres

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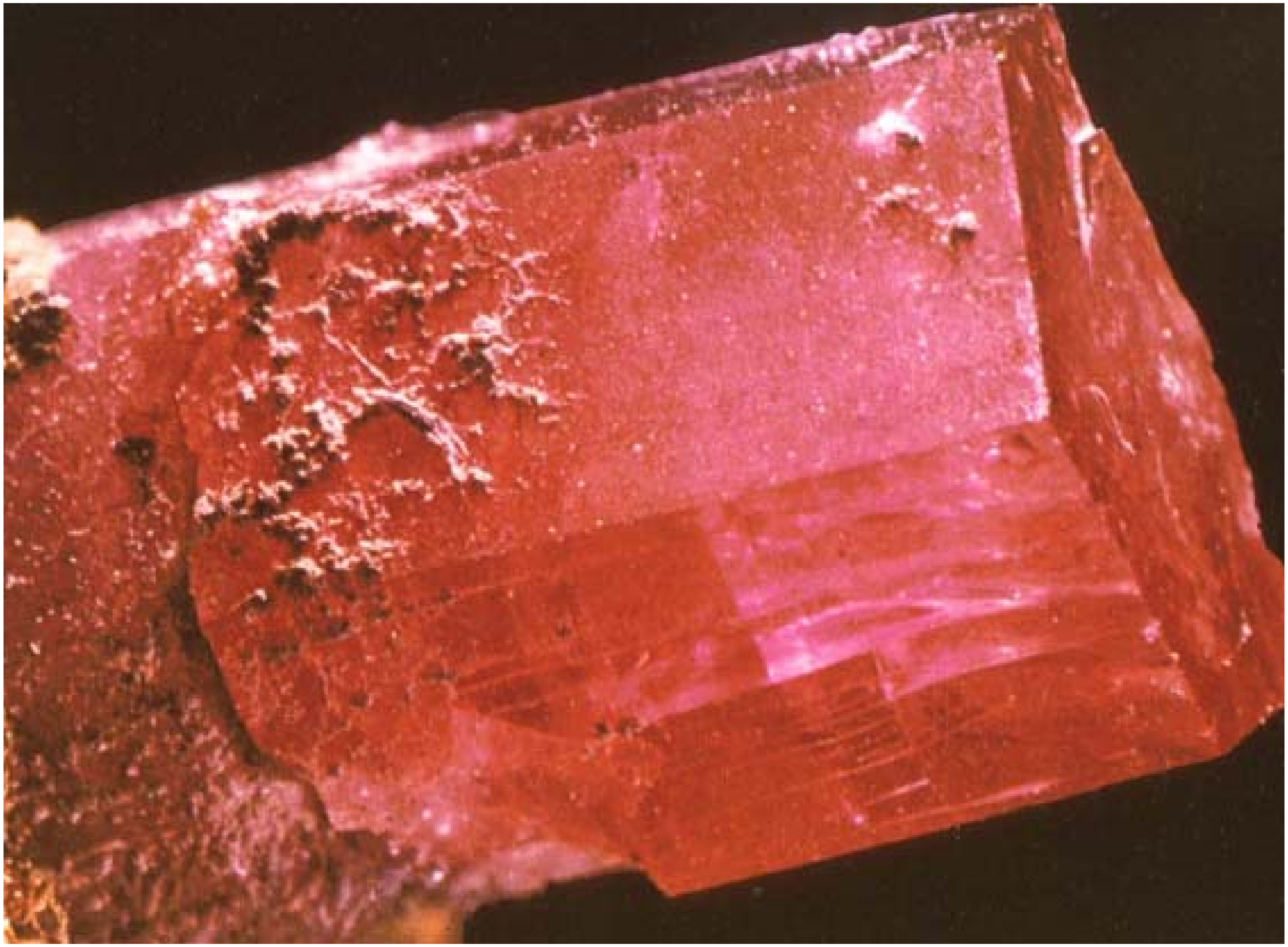
OUTLINE

- Motivation for studying defects in semiconductors
- Optical characterization of materials
- Avogadro project
- Optical Spectroscopy in isotopically pure Si: new information on old systems
- What we want to look at here (^{195}Au)

Quick Demonstration of the effect of impurities in materials I: Al_2O_3:Cr



Quick Demonstration of the effect of impurities in materials II: Al_2O_3:Fe

Defects in semiconductors

- Control of impurities in materials such as semiconductors important, nay vital.

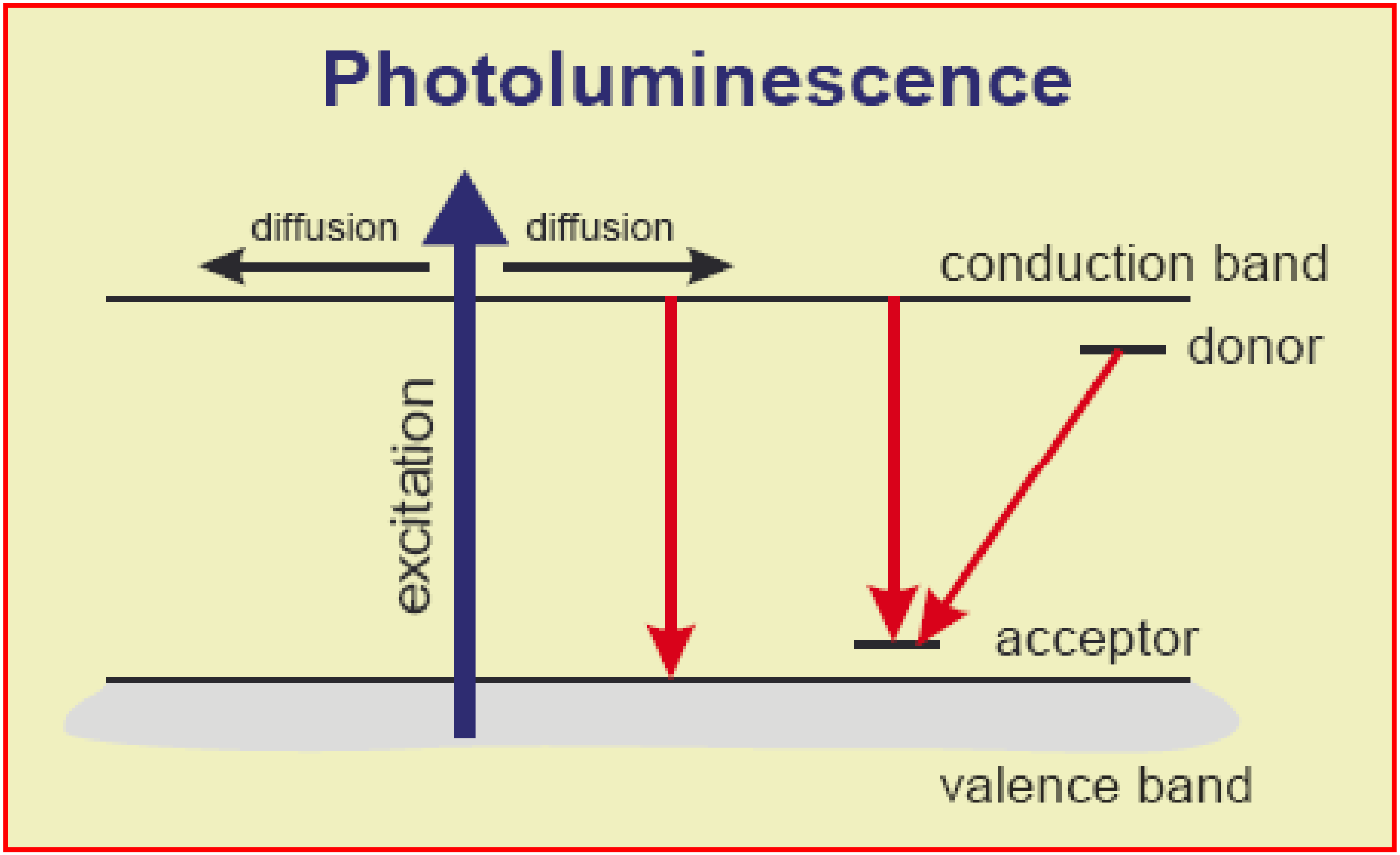
- Recently much of the focus has been on compound semiconductors such as ZnO etc because of their relevance for optoelectronics and new areas such as spintronics.

- Si, although the pre-eminent semiconductor material, shouldn’t be regarded as a closed book.

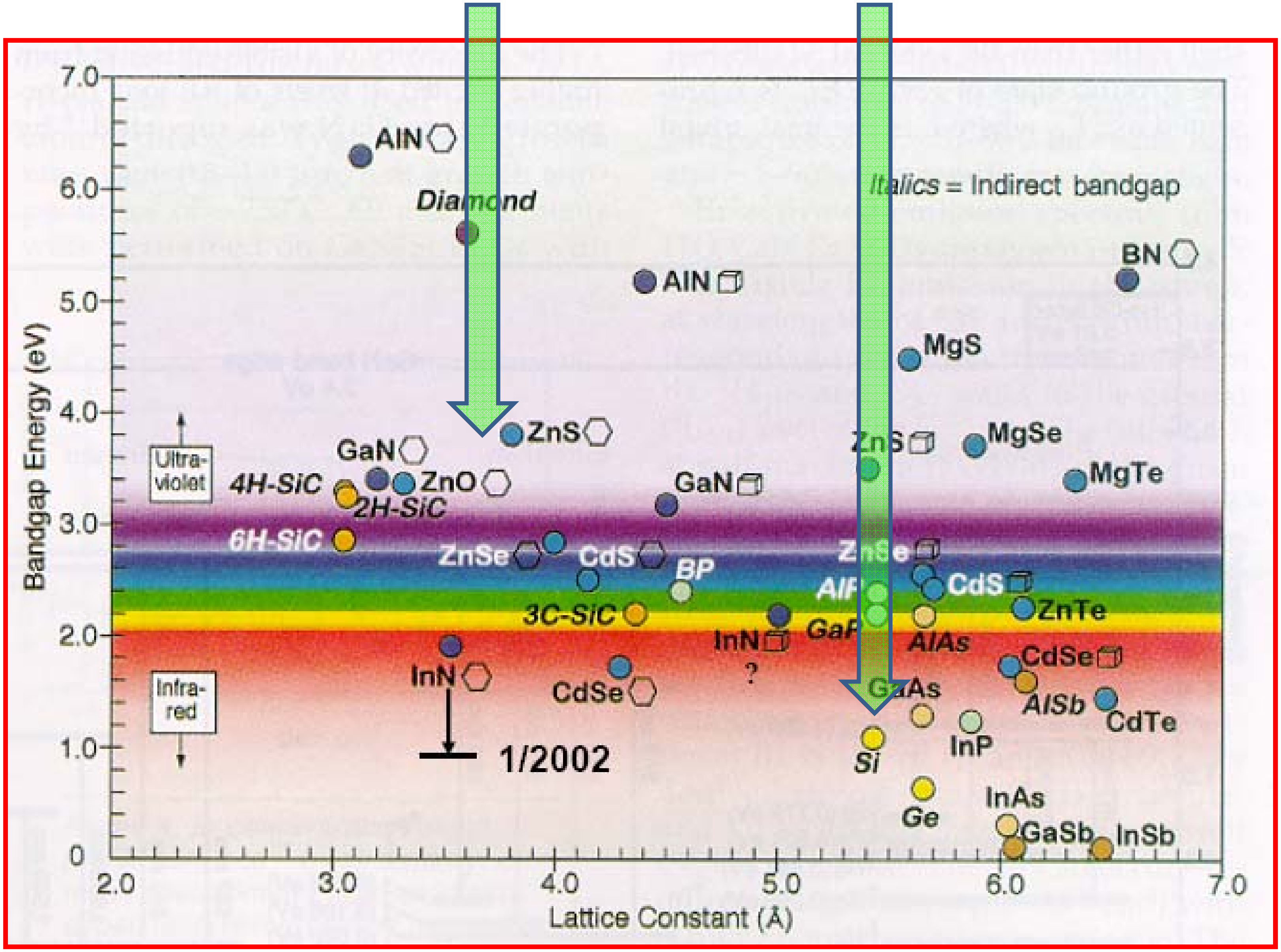
- Experiments using isotopically-pure material are casting new light on old results.

- For the purposes of this proposal the experimental method used will be photoluminescence (PL)

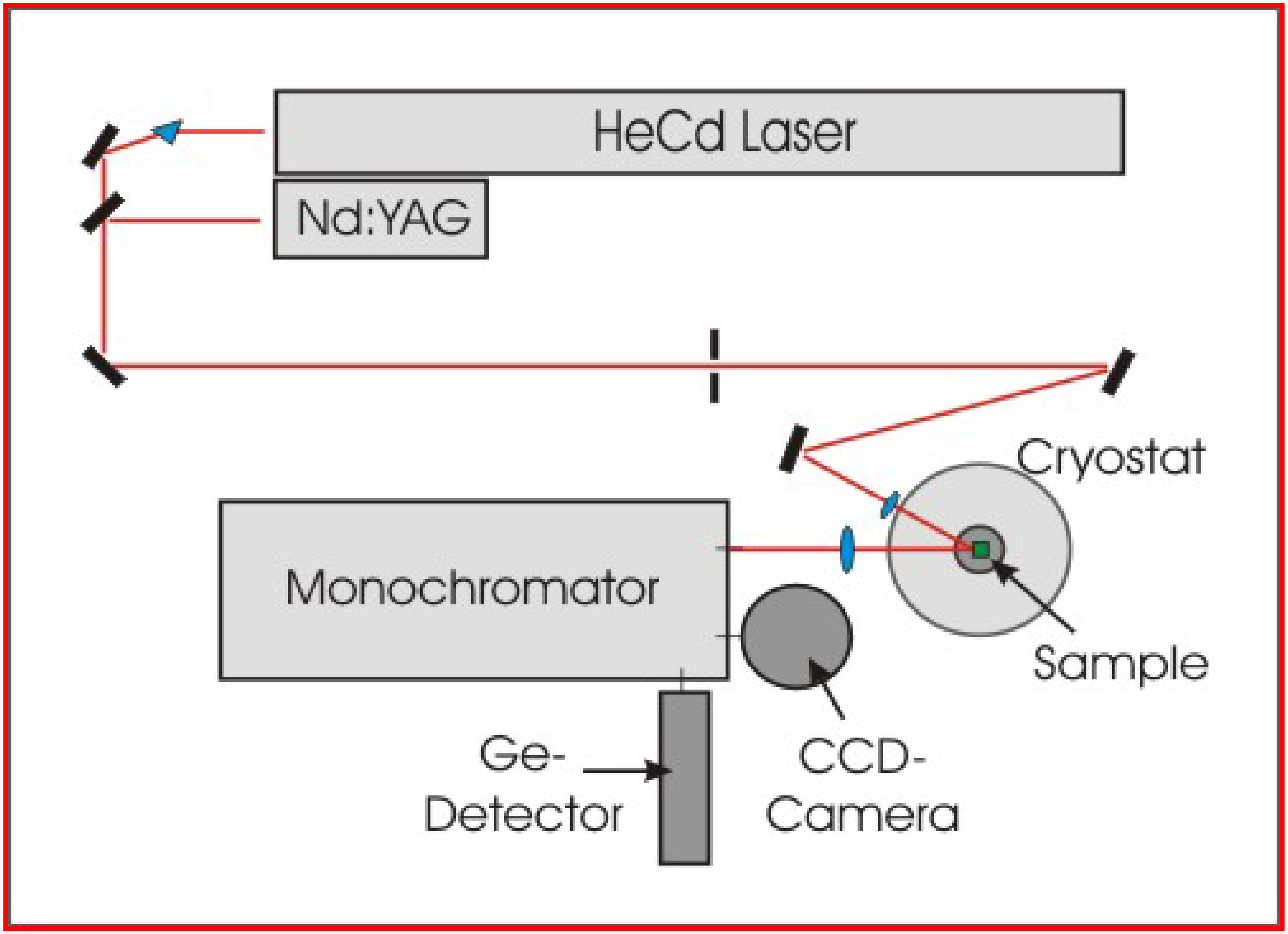
PL Characterisation of Semiconductors



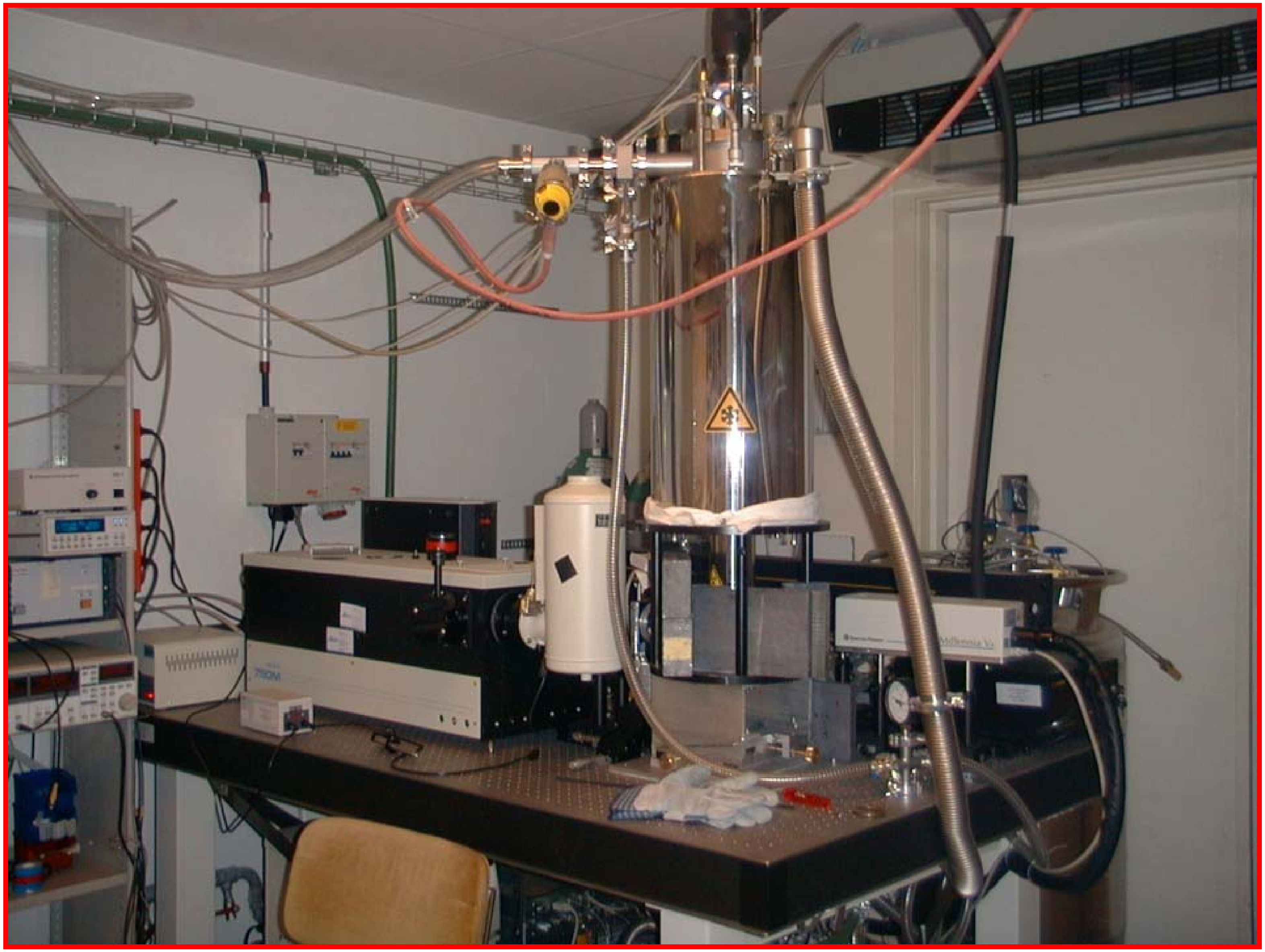
PL Characterisation of Semiconductors



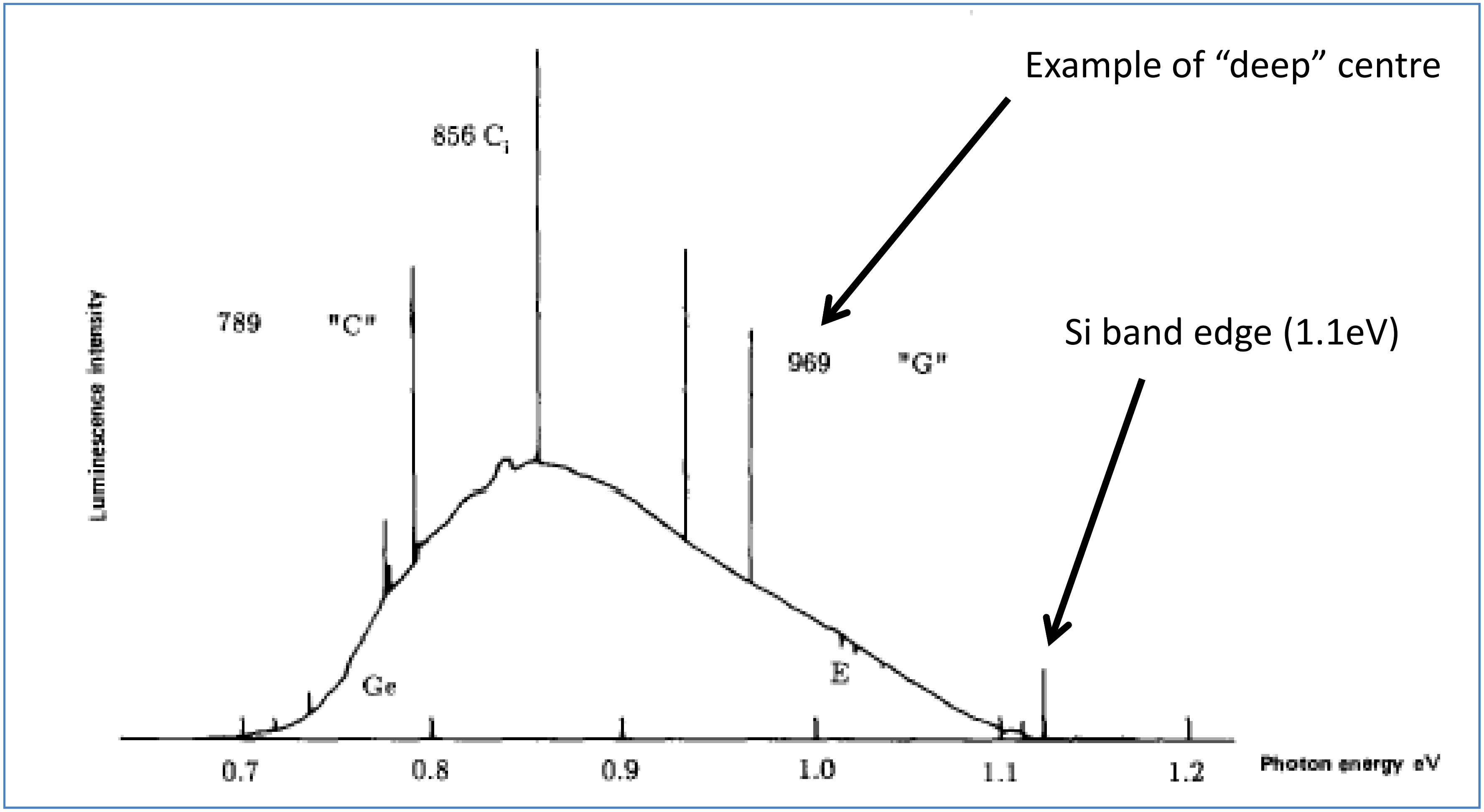
Typical PL apparatus



Typical PL apparatus



Example of typical PL spectrum from Si



Example of “deep” centre

Si band edge (1.1eV)

Taken from Davies Physics Reports ***176*** *3&4(1989)*

Interlude I: Avogadro project

Physical units are now defined in terms of measurable quantities rather than the artifacts of yore.

The remaining exception to this is the kilogram, which is still defined in terms of a Pt-Ir cylinder in Paris.

Now however, there is a project which aims to re-define the kg in terms of the number of atoms of Si in a sphere: the Avogadro project. Desired accuracy 4μg!!!!

Avogadro Project: define kg in terms of number of Si atoms

Count the number of atoms using the X-ray crystal density molar mass method (XRCDMM).

Use a sphere of mono-isotope Si (^{28}Si)

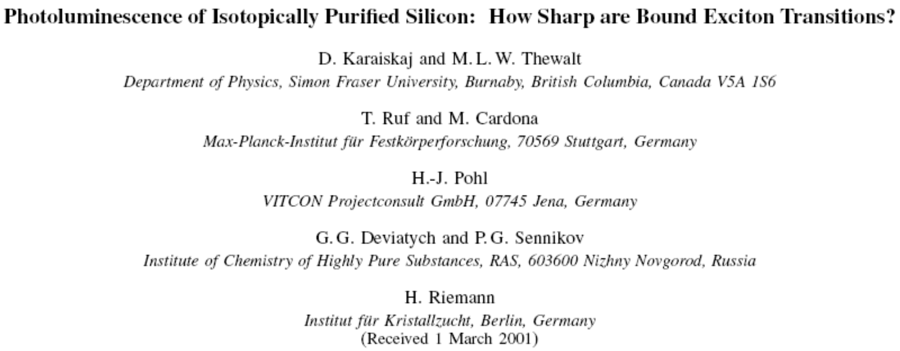
$$N_A = \frac{V_{\mathrm{mol}}}{V_o}.$$

$$N_A = \frac{V_{\mathrm{mol}}}{(a^3/n)},$$

$$N_A = \frac{M_{\mathrm{Si}}}{m}\frac{V}{(a^3/8)},$$

Unexpected by-product of this is being able to study the pure mono-isotope Si using normal optical techniques and see if there are any differences between it and natural material: there are!!!!!!!!

First thing that is striking about the pure material is the sharpness of the optical features



Photoluminescence of Isotopically Purified Silicon: How Sharp are Bound Exciton Transitions?

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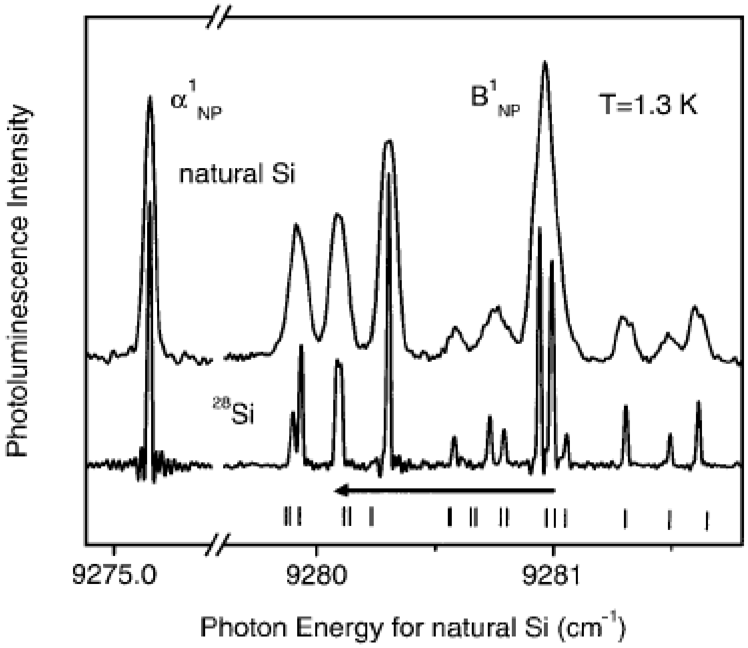
(Received 1 March 2001)

Si normally found in the ratio:
^{28}Si: ^{29}Si : ^{30}Si (92.23 : 4.68 : 3.09)



The pure material has optical features which can't be resolved even with a state of the art Fourier transform spectrometer (0.014cm^{-1}).

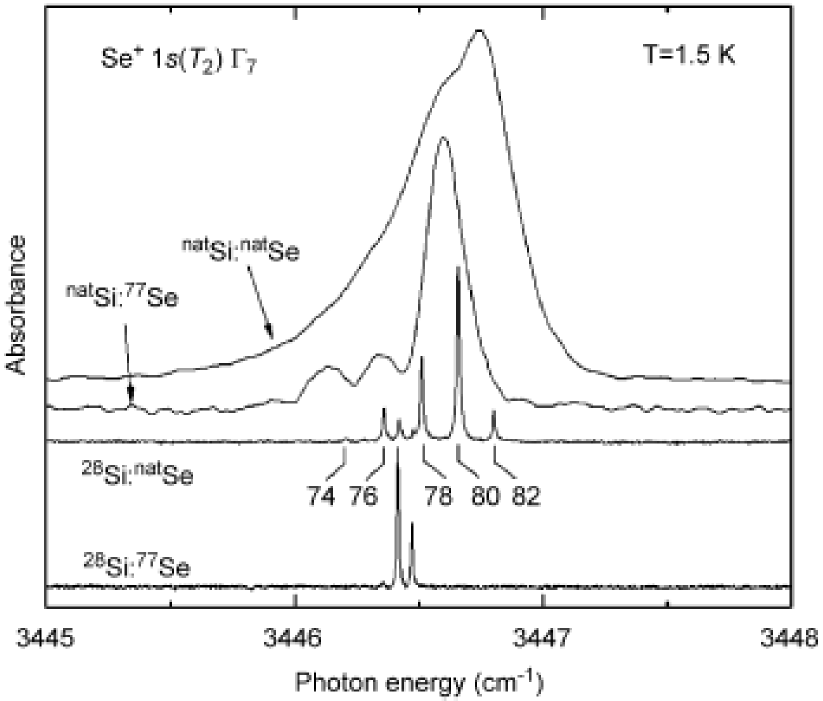
Bound excitons involving P and B sharpen up considerably.

Also get information on the indirect band gap etc, but the real surprise was sharpness of optical features.

Karaiskaj *et al* PRL **86** (26) 2001

This sharpness allows one to see isotopic effects in much more detail than before, and from this, obtain new data.

- Again, similar behaviour for Se, a donor in Si.
- Enables fine structure to be obtained, split in accordance to the natural distribution of Se in nature.
- Also, when utilizing the nuclear spin of ^{77}Se, get hyperfine splitting in the ground state.
- Possible applications in quantum computing?



36	75Kr 4.29 M ϵ: 100.00%	76Kr 14.8 H ϵ: 100.00%	77Kr 74.4 M ϵ: 100.00%	78Kr ≥2.3E+20 Y 0.35% 2ϵ	79Kr 35.04 H ϵ: 100.00%	80Kr STABLE 2.28%	81Kr 2.29E+5 Y ϵ: 100.00%	82Kr STABLE 11.58%	83Kr STABLE 11.49%
	74Br 25.4 M ϵ: 100.00%	75Br 96.7 M ϵ: 100.00%	76Br 16.2 H ϵ: 100.00%	77Br 57.036 H ϵ: 100.00%	78Br 6.46 M ϵ ≥ 99.99% β-≤ 0.01%	79Br STABLE 50.69%	80Br 17.68 M β-: 91.70% ϵ: 8.30%	81Br STABLE 49.31%	82Br 35.282 H β-: 100.00%
34	73Se 7.15 H ϵ: 100.00%	74Se STABLE 0.89%	75Se 119.79 D ϵ: 100.00%	76Se STABLE 9.37%	77Se STABLE 7.63%	78Se STABLE 23.77%	79Se 2.95E+5 Y β-: 100.00%	80Se STABLE 49.61% 2β-	81Se 18.45 M β-: 100.00%
	72As 26.0 H ϵ: 100.00%	73As 80.30 D ϵ: 100.00%	74As 17.77 D ϵ: 66.00% β-: 34.00%	75As STABLE 100%	76As 1.0942 D β-: 100.00%	77As 38.83 H β-: 100.00%	78As 90.7 M β-: 100.00%	79As 9.01 M β-: 100.00%	80As 15.2 S β-: 100.00%
32	71Ge 11.43 D ϵ: 100.00%	72Ge STABLE 27.31%	73Ge STABLE 7.76%	74Ge STABLE 36.73%	75Ge 82.78 M β-: 100.00%	76Ge 1.78E+21 Y 7.83% 2β-	77Ge 11.30 H β-: 100.00%	78Ge 88.0 M β-: 100.00%	79Ge 18.98 S β-: 100.00%
	39		41		43		45		47

Thewalt *et al* Physica B **401-402** 587(2007)

Cu in Si: an old problem

➢Cu is a VERY fast diffuser in Si. At 900C the diffusion coefficient is more than 7 orders of magnitude greater than O_2.

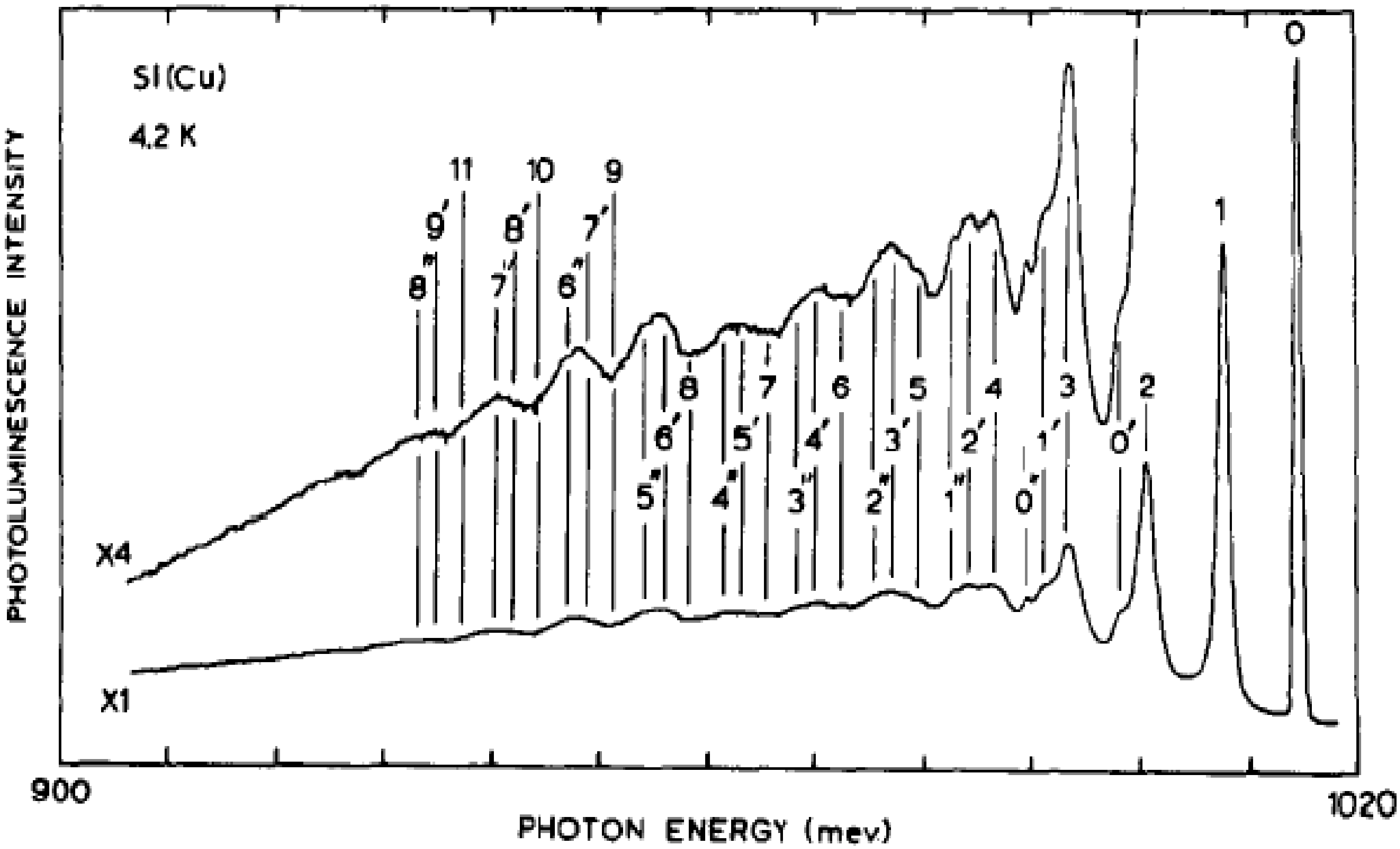
➢As such, it has been a bane on the processing of Si since the 50s; it is nearly always present to some degree.

➢Cu leads to an optical feature at **1014meV**. Triply-degenerate ground state ($\Gamma 4$); doubly-degenerate excited state ($\Gamma 3$).

➢In addition, there is a vibronic sideband with quanta of 7, 16.4 and 25.1 meV which results in a relatively complex spectrum.

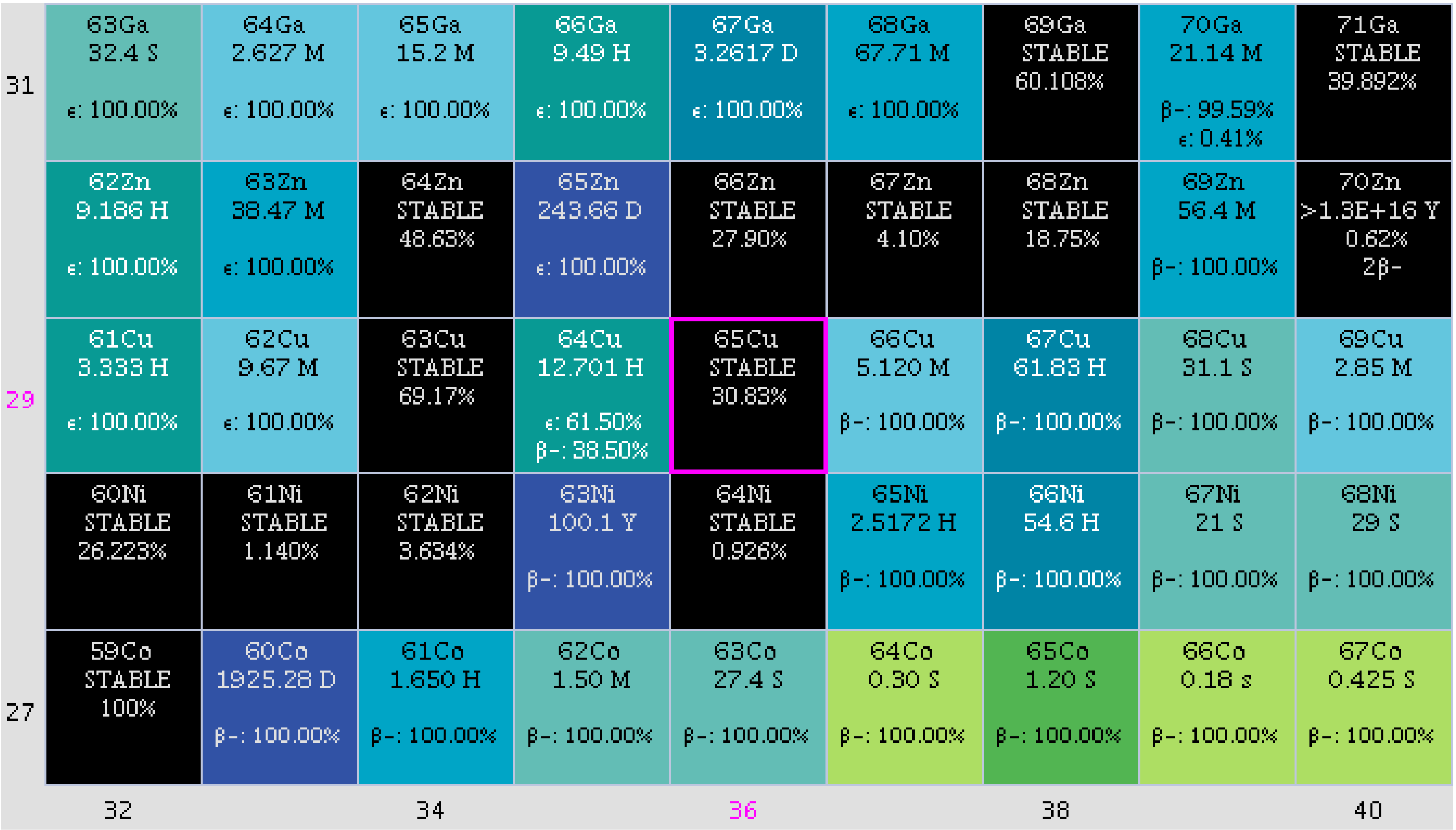
➢The structure of this band has been the subject of quite a bit of work and two competing models are favoured: Cu pair (Cu_s-Cu_i) or a single substitutional Cu centre.

Cu in Si: Typical PL spectrum



Interlude II: Cu isotopes

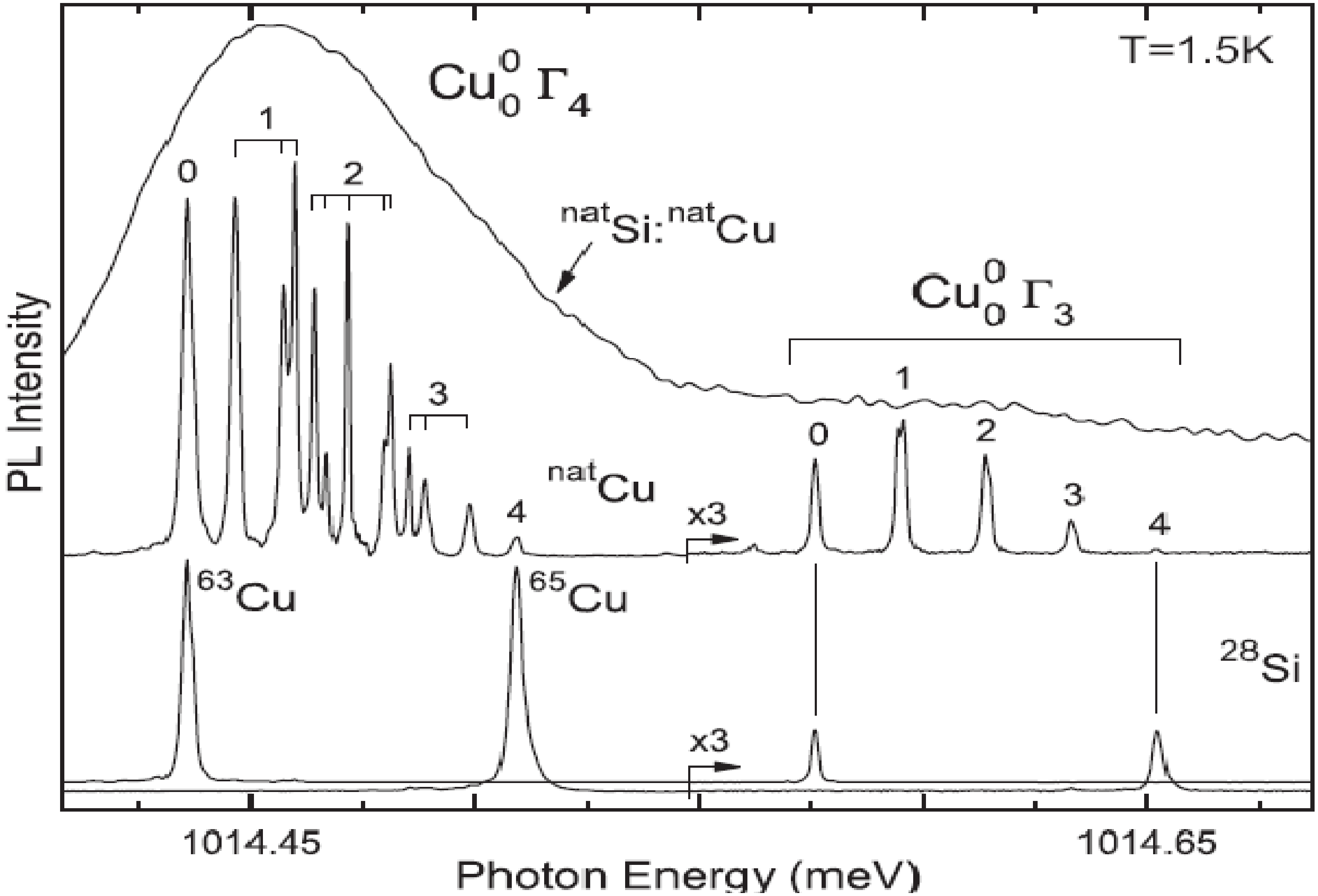
As the lines are so sharp, we can play some games in this pure Si



	32		34		36		38		40
31	63Ga 32.4 S ε: 100.00%	64Ga 2.627 M ε: 100.00%	65Ga 15.2 M ε: 100.00%	66Ga 9.49 H ε: 100.00%	67Ga 3.2617 D ε: 100.00%	68Ga 67.71 M ε: 100.00%	69Ga STABLE 60.108%	70Ga 21.14 M β-: 99.59% ε: 0.41%	71Ga STABLE 39.892%
	62Zn 9.186 H ε: 100.00%	63Zn 38.47 M ε: 100.00%	64Zn STABLE 48.63%	65Zn 243.66 D ε: 100.00%	66Zn STABLE 27.90%	67Zn STABLE 4.10%	68Zn STABLE 18.75%	69Zn 56.4 M β-: 100.00%	70Zn >1.3E+16 Y 0.62% 2β-
29	61Cu 3.333 H ε: 100.00%	62Cu 9.67 M ε: 100.00%	63Cu STABLE 69.17%	64Cu 12.701 H ε: 61.50% β-: 38.50%	65Cu STABLE 30.83%	66Cu 5.120 M β-: 100.00%	67Cu 61.83 H β-: 100.00%	68Cu 31.1 S β-: 100.00%	69Cu 2.85 M β-: 100.00%
	60Ni STABLE 26.223%	61Ni STABLE 1.140%	62Ni STABLE 3.634%	63Ni 100.1 Y β-: 100.00%	64Ni STABLE 0.926%	65Ni 2.5172 H β-: 100.00%	66Ni 54.6 H β-: 100.00%	67Ni 21 S β-: 100.00%	68Ni 29 S β-: 100.00%
27	59Co STABLE 100%	60Co 1925.28 D β-: 100.00%	61Co 1.650 H β-: 100.00%	62Co 1.50 M β-: 100.00%	63Co 27.4 S β-: 100.00%	64Co 0.30 S β-: 100.00%	65Co 1.20 S β-: 100.00%	66Co 0.18 s β-: 100.00%	67Co 0.425 S β-: 100.00%

Cu in ^{28}Si: features sharpen up incredibly.

Spectrum below is a mixture of diffusion and introducing enriched ^{63}Cu and ^{65}Cu.

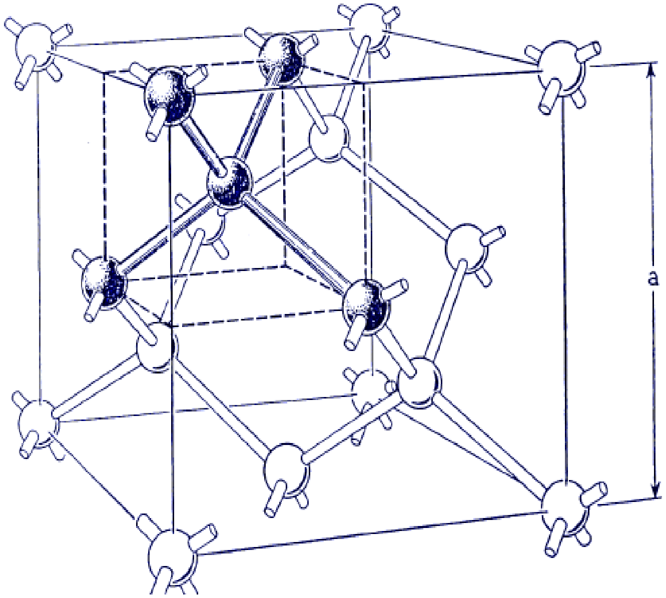


(Thewalt submitted to PRL (2008))

Surprising results!!! Need to re-think our knowledge on deep-levels in Si

The complexity of the results shown can *not* be explained by the previous model of only 2 Cu atoms

Need to invoke *at least* 4 Cu atoms to explain these data, based on the isotopic breakdown etc



These data are new: Exact model still unknown (for that perturbation techniques would be required)

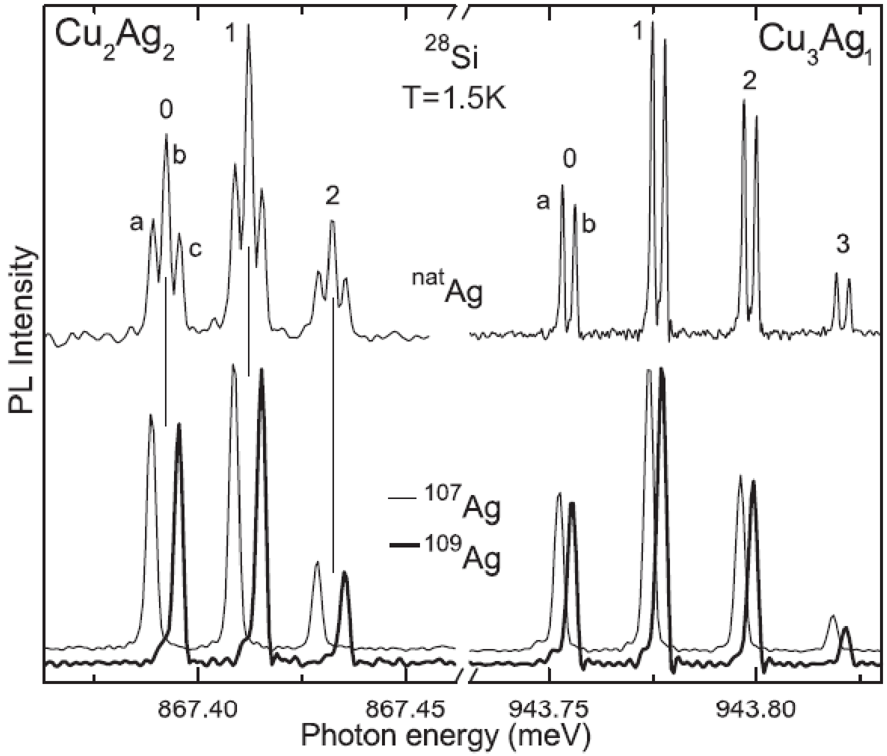
However, it is apparent that metal impurities in Si are perhaps less understood than previously thought.

Look now at Ag and Au

Ag in Si:

Optical feature previously thought to involve *only* Cu is shown to contain Ag also.

In particular 2 Cu atoms and 2 Ag ; 3 Cu and 1 Ag. (additional signal due to 4 Ag atoms).



(Thewalt submitted to PRL (2008))

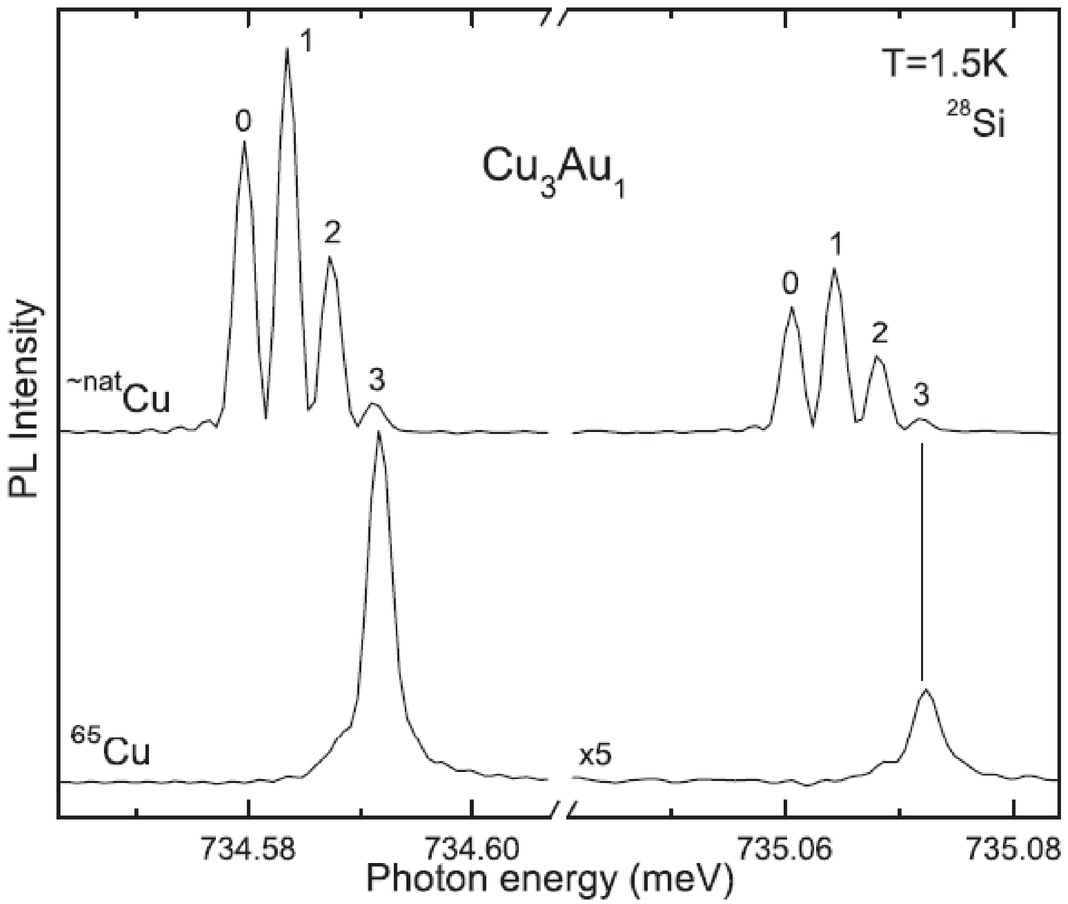
What's the big deal???

These impurities are produced even at low temperatures:

Surprising that complex "families" of impurities can "organize" themselves in this way.

Consequences for future applications of semiconductors: spintronics etc.

Where we'd like ISOLDE to help:



(Thewalt submitted to PRL (2008))

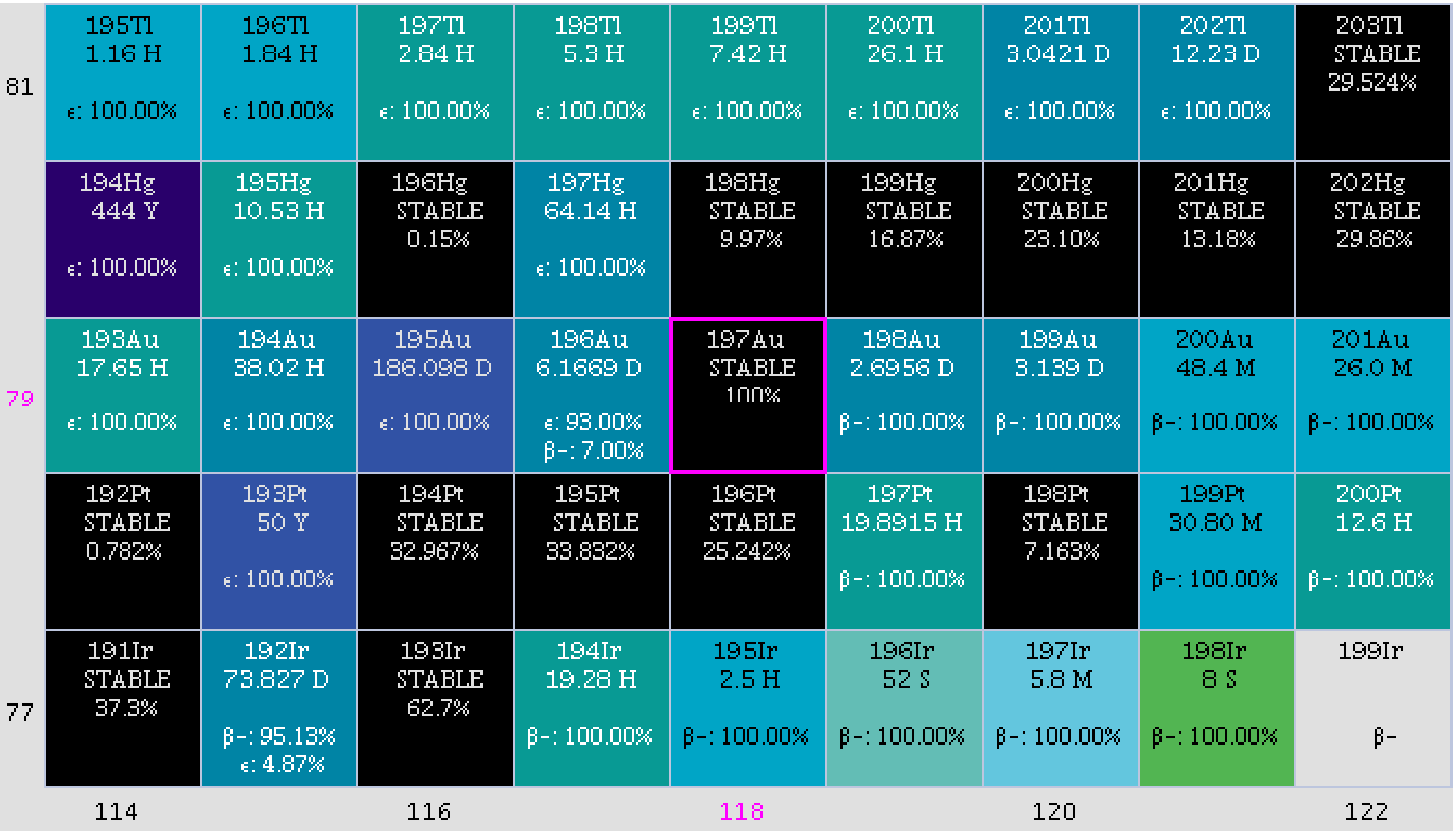
Au is probably the most-studied metallic defect in Si.

A centre previously thought to be due to Fe is revealed to originate from Cu and Au.

Preliminary data suggest that centre is also multi-atom i.e. Cu_3Au, but other possibilities of Au_n are hard to check: why?

Have **Cu_4; Cu_3Ag_1; Ag_4, Cu_3Au; Au_4**????????

Problem: only one stable isotope of Au, but ^{195}Au can be obtained at ISOLDE



81	195Tl 1.16 H ϵ: 100.00%	196Tl 1.84 H ϵ: 100.00%	197Tl 2.84 H ϵ: 100.00%	198Tl 5.3 H ϵ: 100.00%	199Tl 7.42 H ϵ: 100.00%	200Tl 26.1 H ϵ: 100.00%	201Tl 3.0421 D ϵ: 100.00%	202Tl 12.23 D ϵ: 100.00%	203Tl STABLE 29.524%
	194Hg 444 Y ϵ: 100.00%	195Hg 10.53 H ϵ: 100.00%	196Hg STABLE 0.15%	197Hg 64.14 H ϵ: 100.00%	198Hg STABLE 9.97%	199Hg STABLE 16.87%	200Hg STABLE 23.10%	201Hg STABLE 13.18%	202Hg STABLE 29.86%
79	193Au 17.65 H ϵ: 100.00%	194Au 38.02 H ϵ: 100.00%	195Au 186.098 D ϵ: 100.00%	196Au 6.1669 D ϵ: 93.00% β-: 7.00%	197Au STABLE 100%	198Au 2.6956 D β-: 100.00%	199Au 3.139 D β-: 100.00%	200Au 48.4 M β-: 100.00%	201Au 26.0 M β-: 100.00%
	192Pt STABLE 0.782%	193Pt 50 Y ϵ: 100.00%	194Pt STABLE 32.967%	195Pt STABLE 33.832%	196Pt STABLE 25.242%	197Pt 19.8915 H β-: 100.00%	198Pt STABLE 7.163%	199Pt 30.80 M β-: 100.00%	200Pt 12.6 H β-: 100.00%
77	191Ir STABLE 37.3%	192Ir 73.827 D β-: 95.13% ϵ: 4.87%	193Ir STABLE 62.7%	194Ir 19.28 H β-: 100.00%	195Ir 2.5 H β-: 100.00%	196Ir 52 S β-: 100.00%	197Ir 5.8 M β-: 100.00%	198Ir 8 S β-: 100.00%	199Ir β-
	114		116		118		120		122

Request for this proposal

6 shifts of ^{195}Hg → ^{195}Au.

Obtainable through 2 means (as below). Half-life is ~ 186d enables us to do spectroscopy on the isotope as if it were stable. (also radioactive double-check).

Allows several samples to be made, with varying concentrations of ^{195}Au and ^{197}Au.

Samples will then be shipped to Canada for the PL measurements.

Possibility of new data on variety of isotopes in semiconductors may be offered: will require optimizing of the PL system at ISOLDE.

Unique opportunity to probe this new “class: of impurities in Si.

Isotope	Half-life	Implantation energy (keV)	Target	Ion Source
195Hg →195Au→ 195Pt	40h/186d	60 (or less)	Molten Pb	Plasma
195Pb→ 195Ti → 195Hg →195Au→ 195Pt	15m / 186d	60 (or less)	UCx	RILIS