Shallow Impurity Absorption Spectroscopy in Isotopically Enriched Silicon
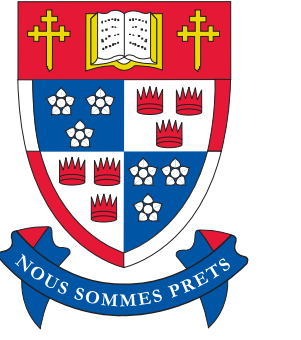
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Introduction

Karaiskaj et al. [1] showed that the *isotopic randomness* present in natural Si (^{nat}Si) causes a significant *inhomogeneous broadening* of many of the long-studied ground state to excited state infrared absorption transitions of the shallow donor phosphorous and acceptor boron. This was surprising since it was thought that the observed linewidths of shallow impurities in silicon are at their fundamental lifetime limit.

We report improved high-resolution infrared absorption studies of these impurities in isotopically enriched ^{28}Si, ^{29}Si and ^{30}Si. The new data improves on the linewidths of earlier spectra [1, 2] particularly in higher excited states due to reduced concentration broadening. *Some of the transitions in ^{28}Si show the narrowest full-width at half-maximum (FWHM) ever reported for shallow donor and acceptor absorption transitions.*

Experimental Method

As compared to previous studies [1, 2] we use *improved samples*:

- ^{28}Si: higher isotopic enrichment, lighter doping
- ^{29}Si & ^{30}Si: higher chemical purity, (but lower isotopic enrichment)

While the chemical purity of the enriched samples is improved, it does not match the purity of ultra-high-purity (UHP) natural silicon samples.

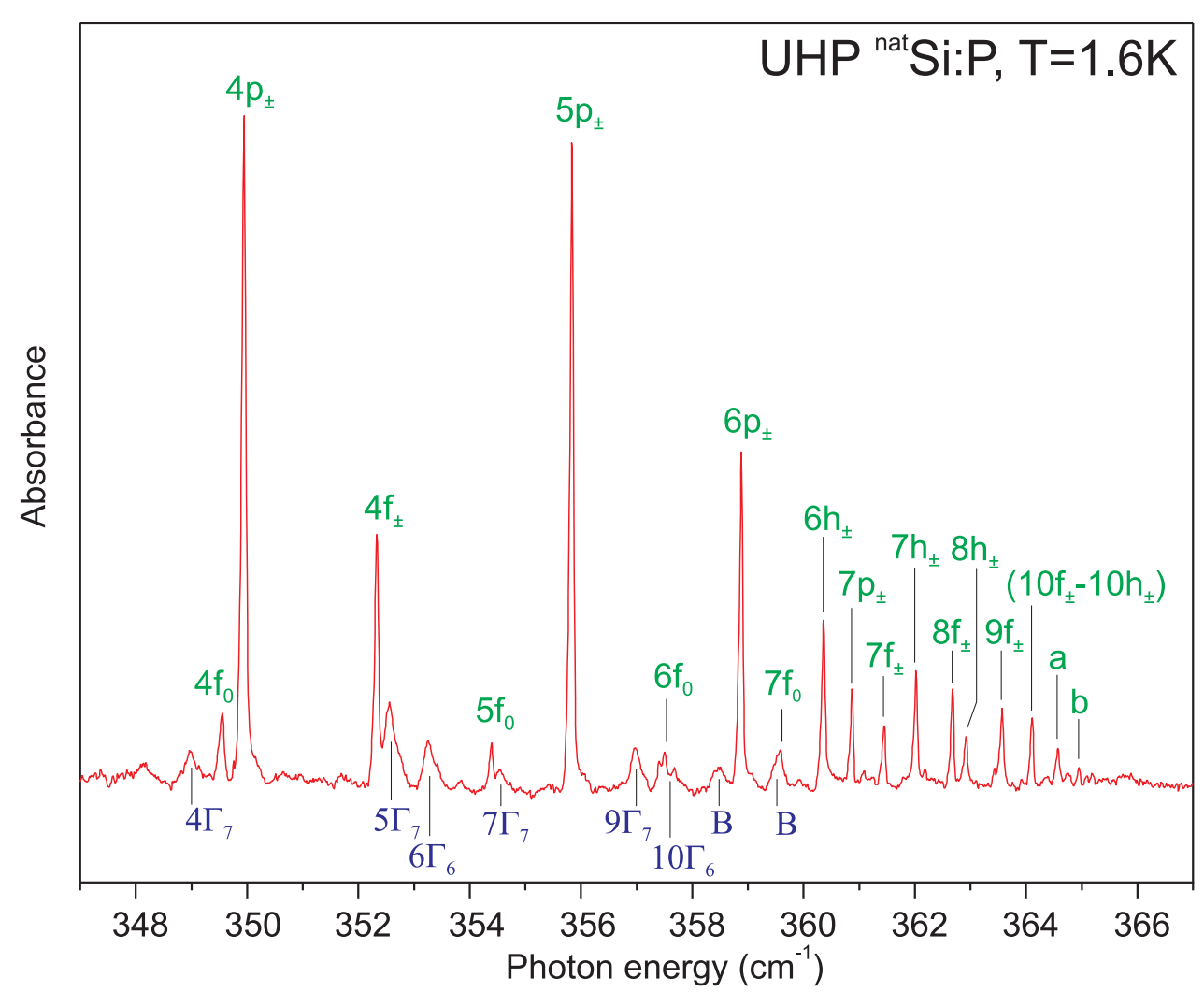|	^{28}Si	^{29}Si	^{30}Si	[P]	[B]
^{28}Si	99.991 %	0.0075 %	0.0015 %	2×10^{12}	5×10^{13}
^{29}Si	4.32 %	91.37 %	4.30 %	2×10^{13}	5×10^{13}
^{30}Si	2.50 %	7.70 %	89.80 %	2×10^{13}	9×10^{13}
^{nat}Si:B	92.2 %	4.7 %	3.1 %	–	3×10^{14}
^{nat}Si:P (UHP)	92.2 %	4.7 %	3.1 %	3×10^{12}	3×10^{12}

Isotopic composition and impurity concentrations (in cm^{-3}) of the samples used here.

Samples: Freely suspended in sample chamber filled with superfluid He, polypropylene windows.
Collection: Bomem DA8.02 fourier transform interferometer.
Detector: Silicon composite bolometer at 1.6 K and Si:B photoconductive detector at 4.2 K.
Resolution: Instrumental resolution 0.012 cm^{-1}.

## Natural Silicon

Phosphorous

For the donor phosphorous in natural Si we report narrower lines and higher excited states than shown before [3, 4, 5, 6]. The $2p_0$ absorption line has a full width at half maximum (FWHM) of 0.082 cm^{-1} and the $7p_\pm$ has a FWHM of only 0.057 cm^{-1}. Our sample also shows two absorption lines for which

IR absorption spectrum of P doped UHP ^{nat}Si at 1.6 K (high energy end).

we could not assign final states and are therefore labeled 'a' and 'b'. All other labels were assigned according to Pajot et al. [7].

Boron

We were also able to obtain an improved spectrum of the acceptor boron in natural silicon, showing higher excited states than published before [8]. Due to the high number of different labeling schemes we attempted to assign labels of theoretically calculated excited states as given by Lewis et al. [8] wherever possible.
Our spectrum clearly shows boron absorption lines up to the $9\Gamma_7$ (labeled 11 in [9]) and $10\Gamma_6$ transitions. Higher energy lines, which could not be assigned to a theoretical level were labeled 'B'.
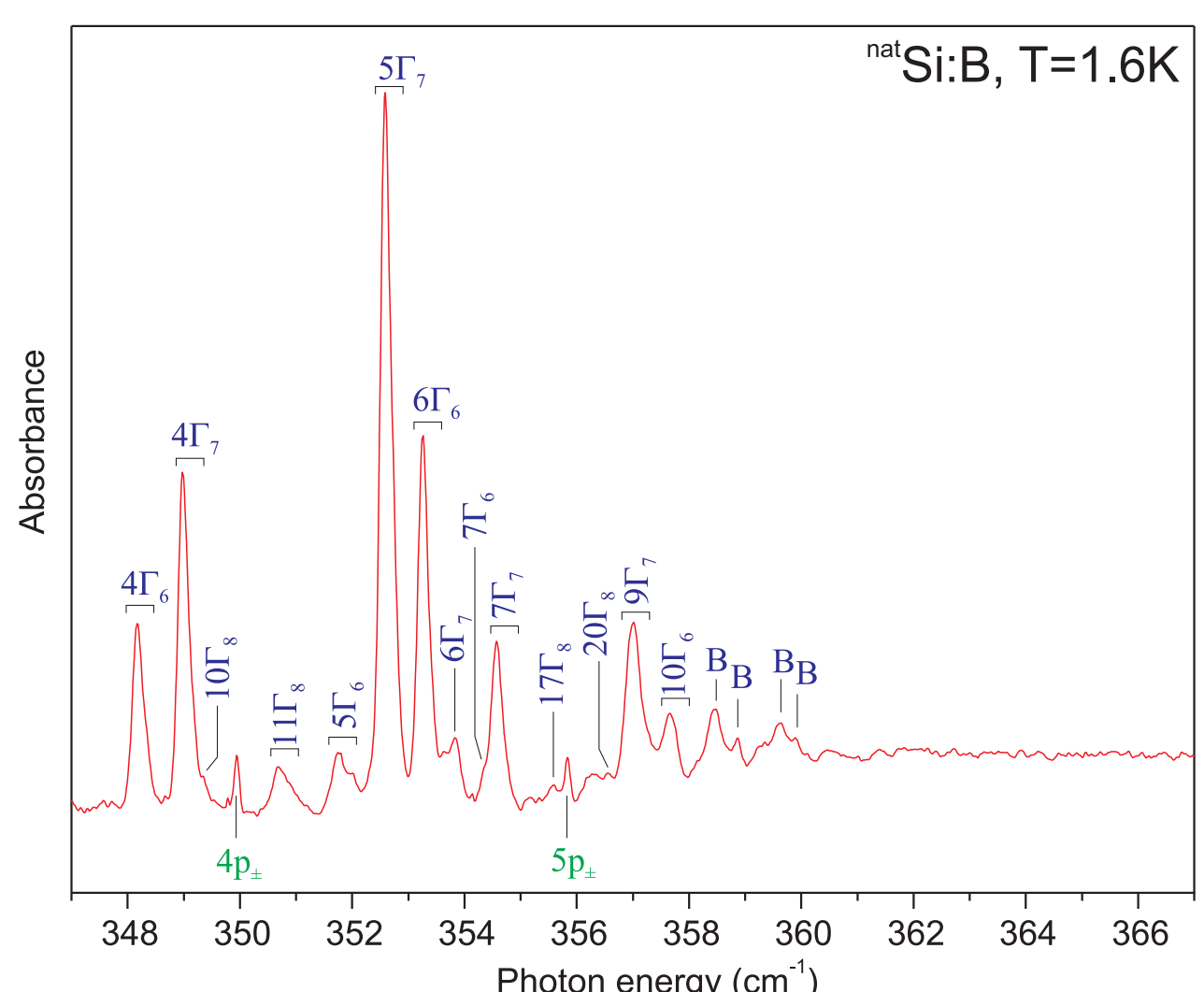
IR absorption spectrum of B doped ^{nat}Si at 1.6 K (high energy end).

Isotopically Enriched ^{28}Si
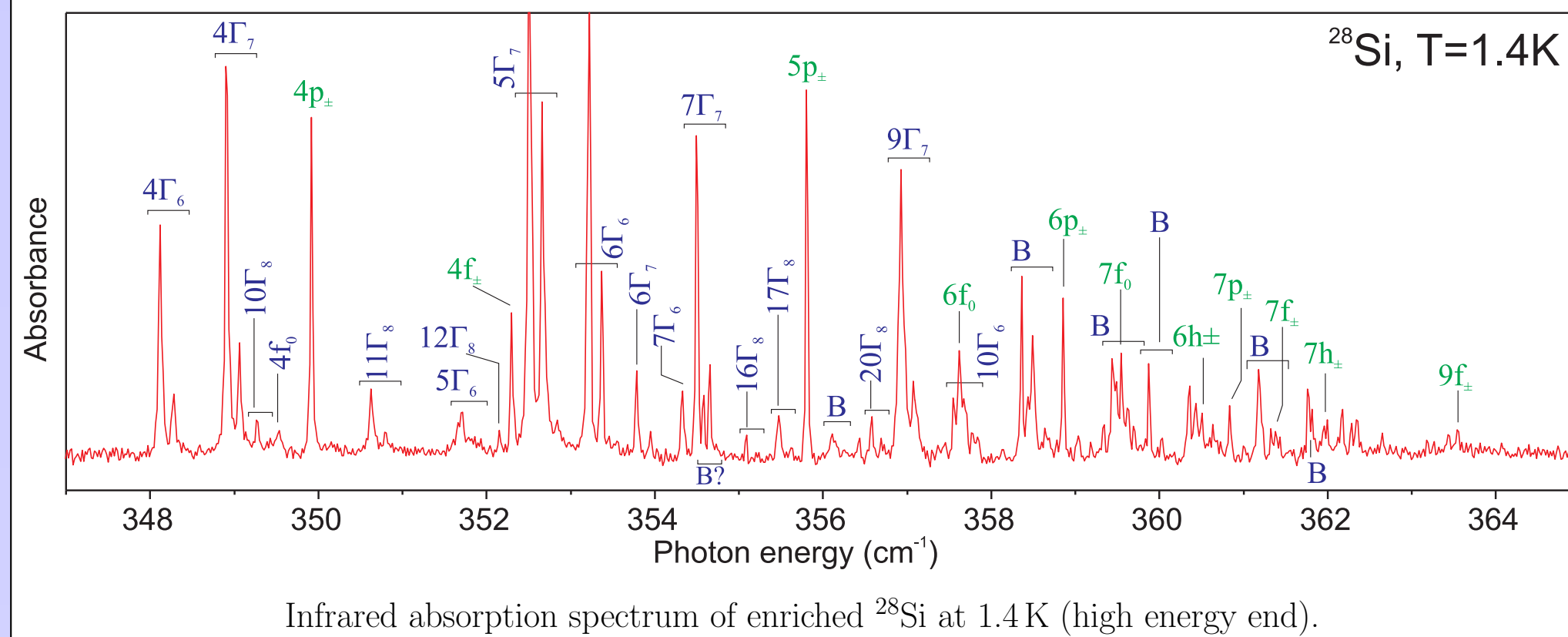
Infrared absorption spectrum of enriched ^{28}Si at 1.4 K (high energy end).

Phosphorous

In previous publications [1] on isotopically enriched ^{28}Si mainly the low energy absorption lines of the donor phosphorous were found to be sharper than in ^{nat}Si due to concentration broadening of higher excited states. Here we report *narrower linewidths for many of the high energy transitions*.

Boron

Thanks to the reduction of concentration broadening we have observed narrower absorption lines for the acceptor boron, as well.
Many of the boron transitions reveal a 0.15 cm^{-1} splitting in ^{28}Si which was attributed to the difference in binding energy between ^{10}B and ^{11}B acceptors [1]. The doublet intensity ratio reflects the ^{11}B/^{10}B natural abundance ratio of ∼ 80/20.

	P				B			
	$2p_0$	$4p_\pm$	$\mathbf{5p_\pm}$	$6p_\pm$	$3\Gamma_7$	$4\Gamma_6$	$\mathbf{6\Gamma_6}$	$7\Gamma_7$
observed	0.033	0.029	**0.022**	0.023	0.048	0.040	**0.025**	0.025
actual	0.031	0.026	**0.019**	0.020	0.046	0.038	**0.022**	0.022
vs. ^{nat}Si	up to 5× narrower[a]				up to 10× narrower[b]			

FWHM for selected lines in ^{28}Si in cm^{-1}. The actual FWHM takes the instrumental resolution of 0.012 cm^{-1} into account. Factors vs. ^{nat}Si as compared to the narrowest reported FWHM in a) [6] and b) [8].

Line Broadening

The broadening seen in ^{nat}Si or any sample of mixed isotopic composition is dominated by an effect which is independent of the small shifts in binding energy between pure ^{28}Si, ^{29}Si and ^{30}Si (see below).
The wave function of the ground state is relatively compact, so in samples with mixed isotopes individual impurities can have signigicantly different local isotopic compositions. These fluctuations induce shifts (and splittings for acceptors) of the ground states, which can be related to the known shifts of valence and conduction band energies with average isotopic composition. The excited state wave functions are much more extended and therefore sample an isotopic composition closer to the average.
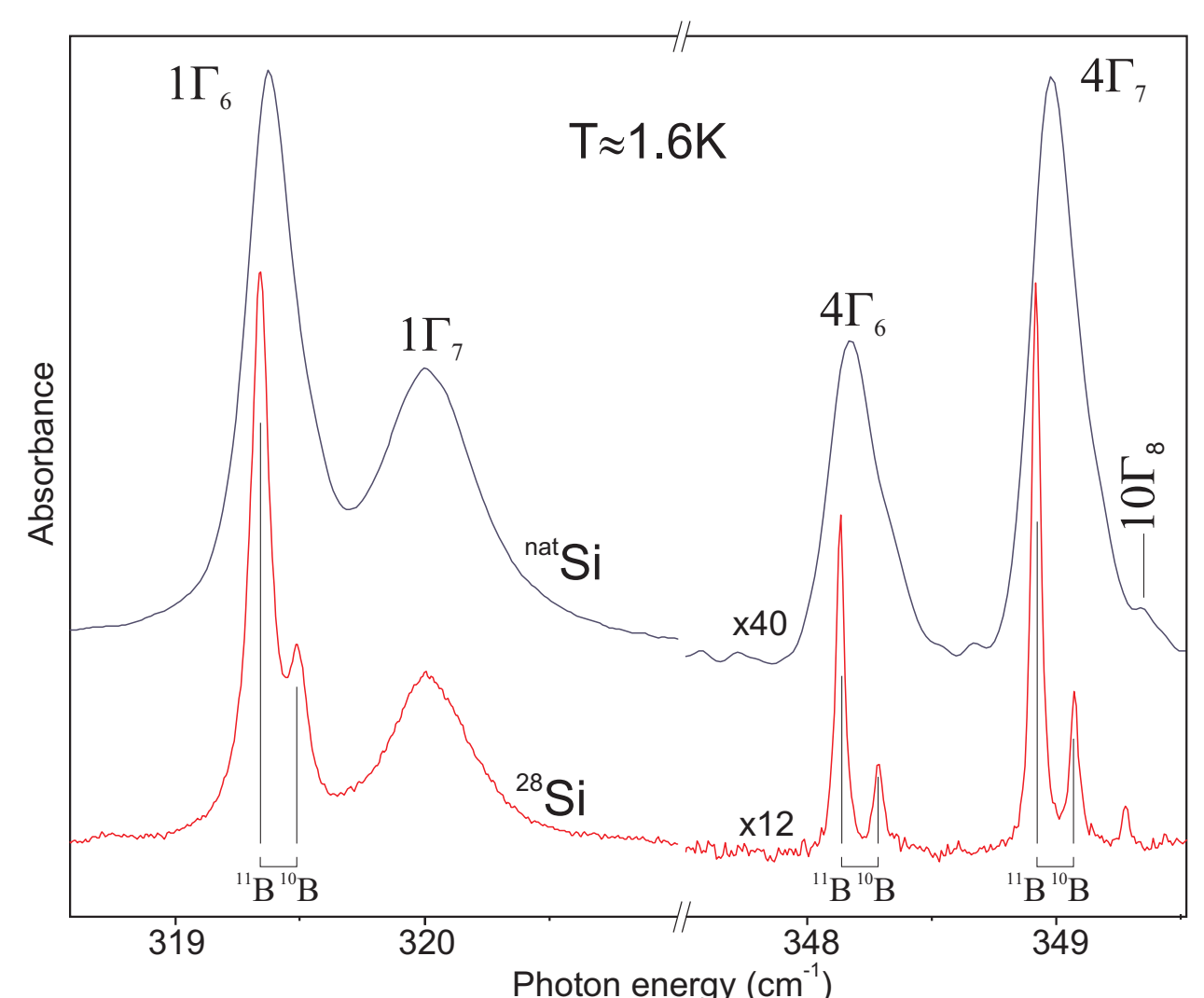*The difference in isotopic composition sampled by excited and ground state results in inhomogeneous broadening.* The valence band shifts more than the conduction band [10] causing a stronger broadening for the acceptor B than for the donor P.

Comparing ^{28}Si and ^{nat}Si

For comparison the high energy end of the absorption spectra of ^{28}Si and ^{nat}Si are overlayed here. The line sharpening and the additional detail as well as the shift of the acceptor absorption lines can be seen.
We suspect that the line labeled $9\Gamma_7$ is actually composed of two overlaid ^{11}B/^{10}B doublets.
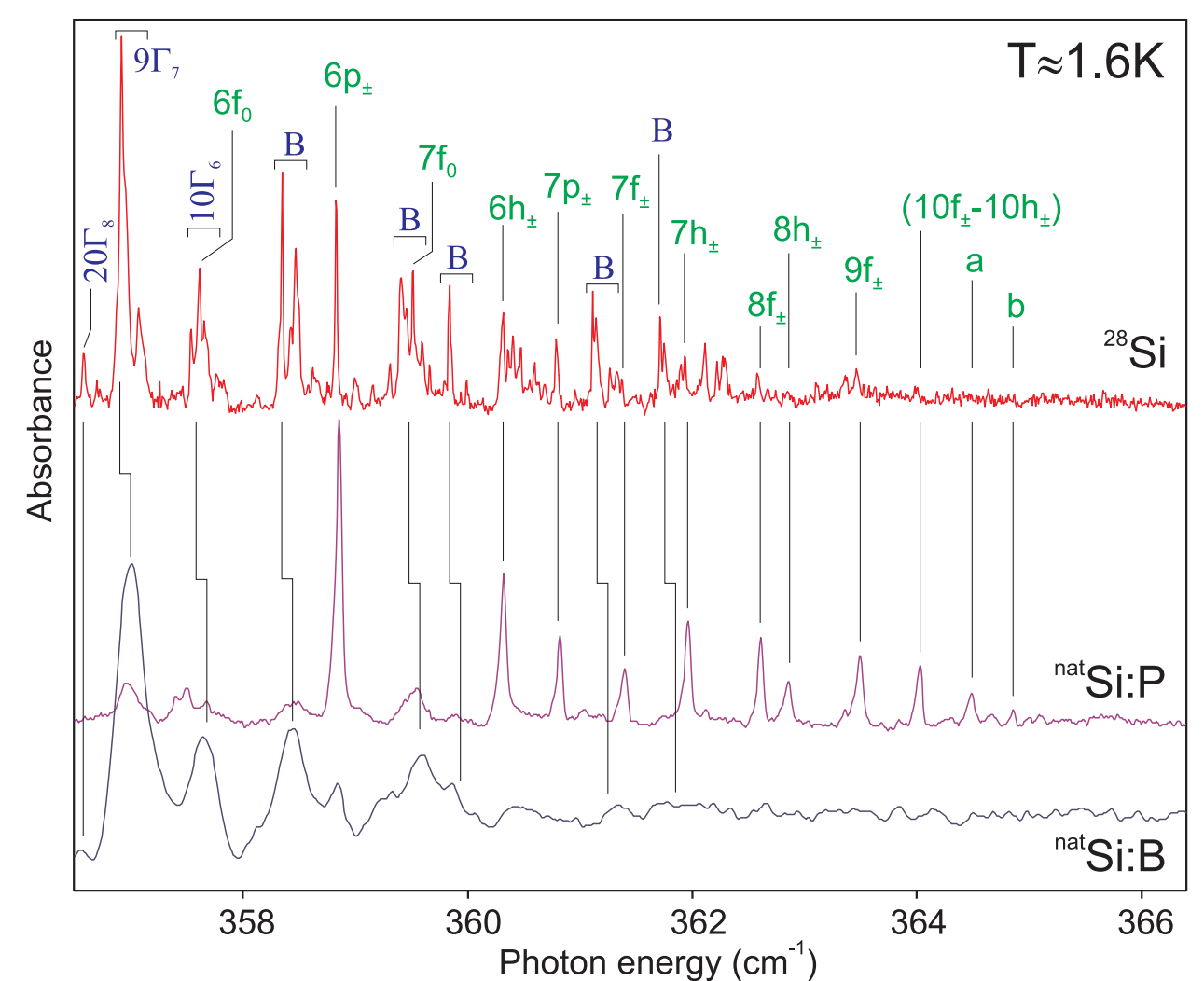
Comparison of the enriched ^{28}Si spectrum to phosphorous and boron doped natural silicon.

The second spectrum shows that some absorption lines reveal the ^{11}B/^{10}B splitting while others are dominated by *lifetime broadening* even in ^{nat}Si. Some transitions like $1\Gamma_8$ show a significant lifetime broadening with no further reduction of their linewidths in ^{28}Si.
This lifetime broadening effect was explained by Kane [11] and confirmed by Barrie and Nishikawa [12, 13] as a result of transitions to other nearby excited states involving acoustic phonons.

Absorption lines like $4\Gamma_6$ and $4\Gamma_7$ sharpen up significantly while others like $1\Gamma_7$ has a life time limited line width. The brackets indicate the ^{11}B/^{10}B splitting (∼ 80%/20%).

Binding Energy Shifts

Theory

E_B, the ionization energy for shallow (hydrogenic) levels in semiconductors can be scaled to the hydrogen Rydberg Ry:

$$E_B = Ry \cdot m^*/\epsilon_0^2$$

While this equation is too simple to provide accurate values of impurity binding energies, it can be used to estimate the shift in E_B with isotopic composition from the dependence on m^* and ϵ_0. Donor and acceptor binding energies scale identically with the dependence of ϵ_0 on M. In Si, the contribution of both ϵ_0 and m^* act to increase the binding energy with increasing isotopic mass [2].

Experiment

Here we compare the shifts in the binding energy E_B among the different samples. Our new, improved data allows us to determine those shifts more accurately than before [2] and shows that the previously determined shifts (old δE) were overestimated due to broadening and splitting of the lines in earlier ^{29}Si and ^{30}Si samples.

	P				B			
	$2p_\pm$	$6p_\pm$	$8f_\pm$	E_B	$1\Gamma_8$	$1\Gamma_6$	$5\Gamma_7$	E_B
δE	-0.100	-0.129	-0.134	-0.15	-0.264	-0.350	-0.407	-0.44
old δE				-0.32				-0.73

Energy shifts (in cm^{-1}) for different transitions between ^{28}Si and ^{30}Si with $\delta E = E(^{28}$Si$) - E(^{30}$Si$)$. e_B is the estimated shift in binding energy between pure ^{28}Si and pure ^{30}Si.
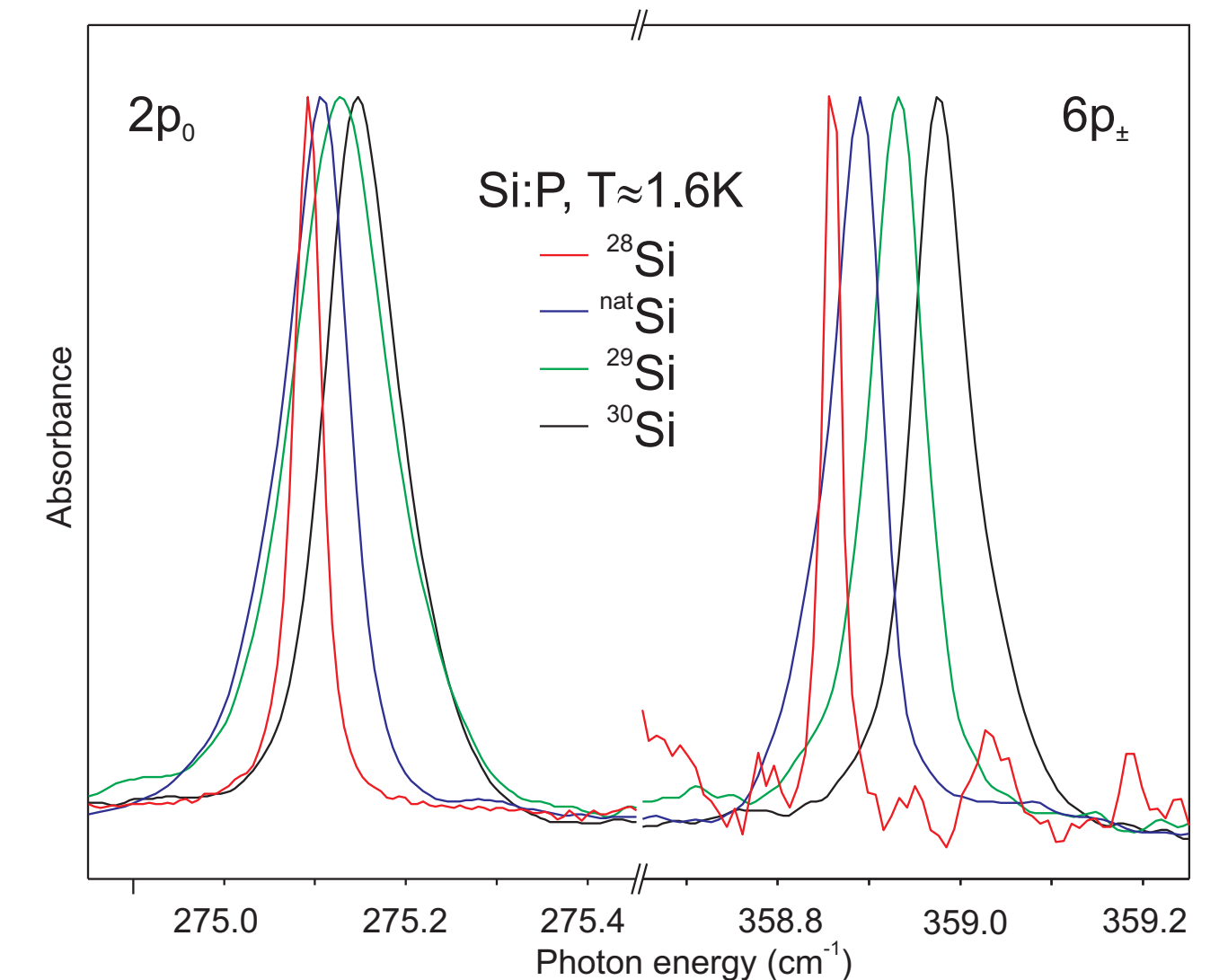
Comparison of the $2p_0$ and $6p_\pm$ lines in ^{28}Si, ^{nat}Si, ^{29}Si and ^{30}Si.

The figures show the shifts for two representative P and B transitions in ^{28}Si, ^{nat}Si, ^{29}Si and ^{30}Si, respectively. The dependence of ϵ_0 and m^* on the isotopic mass scales the ground state and excited state binding energies by an identical factor, and thus the largest shifts are observed for transitions to the highest excited states.
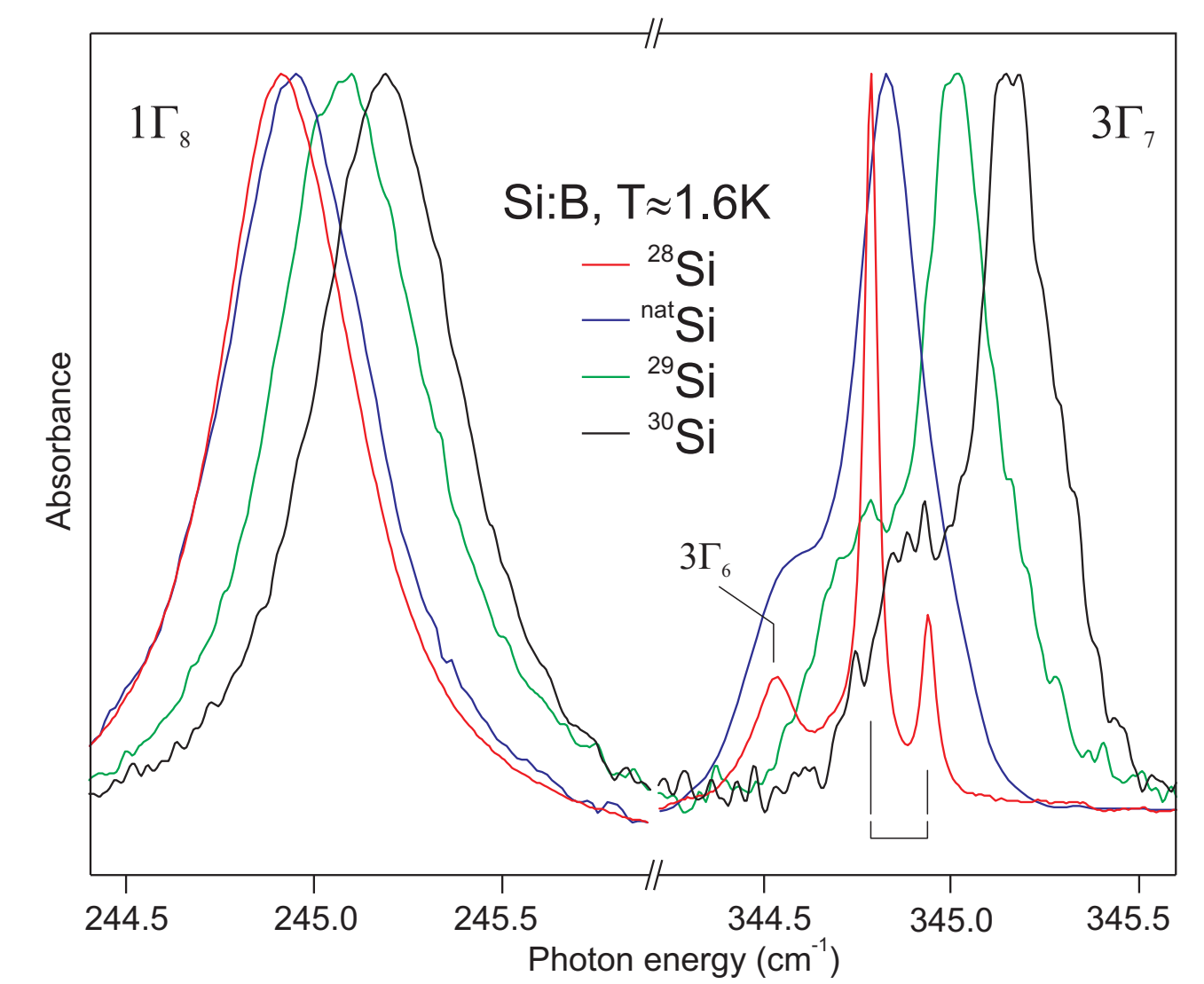
Comparison of the $1\Gamma_8$, $3\Gamma_6$ and $3\Gamma_7$ lines in ^{28}Si, ^{nat}Si, ^{29}Si and ^{30}Si.

Acknowledgments

References

[1] D. Karaiskaj, J. A. H. Stotz, T. Meyer, M. L. W. Thewalt, and M. Cardona. *Phys. Rev. Lett.* **90**(18), 186402 (2003).

[2] D. Karaiskaj, T. A. Meyer, M. L. W. Thewalt, and M. Cardona. *Phys. Rev. B* **68**(12), 121201 (2003).

[3] C. Jagannath, Z. W. Grabowski, and A. K. Ramdas. *Solid State Commun.* **29**, 4 (1979).

[4] C. Jagannath, Z. W. Grabowski, and A. K. Ramdas. *Phys. Rev. B* **23**, 2082 (1981).

[5] B. Pajot, J. Kauppinen, and R. Anttila. *Solid State Commun.* **31**, 759 (1979).

[6] B. A. Andreev, E. B. Kozlov, and T. M. Lifshits. *Mat. Sci. Forum* **196-201**, 121 (1995).

[7] B. Pajot, G. Grossmann, M. Astier, and C. Naud. *Solid State Commun.* **54**(1), 57 (1985).

[8] R. A. Lewis, P. Fisher, and N. A. McLean. *Aust. J. Phys.* **47**, 329 (1994).

[9] D. W. Fischer and J. J. Rome. *Phys. Rev. B* **27**(8), 4826 Apr (1983).

[10] D. Karaiskaj, G. Kirczenow, M. L. W. Thewalt, R. Buczko, and M. Cardona. *Physical Review Letters* **90**(1), 016404 (2003).

[11] E. O. Kane. *Physical Review* **119**(1), 40–42 (1960).

[12] K. Nishikawa and R. Barrie. *Can. J. Phys* **41**, 1135 (1963).

[13] R. Barrie and K. Nishikawa. *Can. J. Phys* **41**, 1823 (1963).