



Isotope effects in the electronic spectra of singly ionised S^+ and Se^+ donors in silicon

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Abstract

We report on the observation of weak satellites of the strong and sharp parity-forbidden, but symmetry-allowed $1s(A_1) \rightarrow 1s(T_2)$ doublet of the infrared electronic spectrum of S^+ in silicon. The low-energy satellites are ascribed to a Si isotope effect and the high-energy ones to an S isotope effect. We also show that the profile of the low-energy component of the same transition of Se^+ can be reproduced from the computed combination of Si and Se isotope effects with the same global characteristics as those of S^+ . These shifts are discussed in terms of the effect of the Si-chalcogen bond softening in the electronic ground state and of a Jahn–Teller coupling of the electronic excited state with a triply degenerate vibrational mode of a cluster involving the chalcogen atom and its first nearest neighbours. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Isotope shifts (ISs) of electronic lines are usually seen in high-energy photoluminescence or absorption spectra. They are related to the coupling of the electronic levels to local vibrational modes with zeroth-order isotope effects. They reflect the contribution of the zeroth-order vibrational IS to the zero-point energies of the ground and excited electronic states. At a difference with the vibrational ISs, the electronic ISs can be positive or negative and the prediction of these shifts requires

detailed analyses of the dynamic structures of the centres.

In silicon, substitutional S and Se atoms have two more valence electrons than Si. The binding energy of the first electron of S in silicon is rather large (~ 0.3 eV) compared to P and As (~ 0.05 eV), but within shifts of their positions, the electronic line spectra of S^0 , Se^0 , P and As are strikingly similar as they involve effective mass-like excited states. The $1s$ state displays the six-fold degeneracy of the minimum of the conduction band of silicon, but the degeneracy is lifted by a central-cell effect and the singlet $1s(A_1)$ state can be substantially deeper than the $1s(E)$ and $1s(T_2)$ states. The IR absorption of the symmetry-allowed $1s(A_1) \rightarrow 1s(T_2)$ doublet of Bi has been observed

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in silicon [1] (the doublet structure is due to a spin-valley coupling made possible by the p character of the T_2 levels). The ground state of the second electron of S and Se is near 0.6 eV. The line spectra of S^+ and Se^+ bear similarities with those of S^0 and Se^0 , but the line spacing between corresponding lines is four times larger for S^+ and Se^+ [2].

Besides an H/D isotope effect due to tunnelling differences between H and D in a donor complex in germanium [3], no isotope effect of effective mass-like donor and acceptor spectra has been reported in semiconductors. We present here results showing the existence of two distinct ISs of the $1s(A_1) \rightarrow 1s(T_2)$ doublet of S^+ in silicon [4]. We discuss them in terms of the coupling of this ion with its nearest neighbours and we extrapolate to the case of Se^+ ion.

2. Experimental results

The sample was prepared from float-zone B-doped silicon. The spectra were obtained with a BOMEM DA8 FT spectrometer with an optical filter (high-frequency cut-off at 0.7 eV) inserted between the quartz-halogen source and the sample.

The doublet structure of $1s(T_2)$ is shown in Fig. 1 (we omit the ground state). The lowest energy line corresponds to the two-dimensional

representation Γ_7 of the T_d double group and the highest energy one to the four-dimensional representation Γ_8 . The sharpness and intensity of this doublet allow to detect satellites for both components. Components L_1 and L_2 are similar to those due to the vibrational Si isotope effect [5]. They could then be due to a Si isotope effect as substitutional S has four nearest Si neighbours. In the same way, component H_1 could be due to the ^{34}S isotope as $[^{34}\text{S}]/[^{32}\text{S}]$ is 0.045. A contribution of ^{33}S would lie midway between the ^{32}S and ^{34}S components, but its absence can be explained by the value of 0.008 for $[^{33}\text{S}]/[^{32}\text{S}]$ in natural sulphur and the high-energy onset of the strong ^{32}S line.

We can substantiate the Si isotope guess by considering a SSi_4 cluster interacting weakly with the crystal. From the natural abundances of ^{28}Si , ^{29}Si and ^{30}Si (0.922, 0.047 and 0.031, respectively), the four most probable surroundings of an S atom are $^{28}\text{Si}_4$, $^{28}\text{Si}_3^{29}\text{Si}$, $^{28}\text{Si}_3^{30}\text{Si}$ and $^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$. The ratios of the probabilities of the $^{28}\text{Si}_3^{29}\text{Si}$, $^{28}\text{Si}_3^{30}\text{Si}$ and $^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$ surrounding combinations normalised to $^{28}\text{Si}_4$ are 0.20, 0.13 and 0.02, respectively. They compare with the measured values of 0.21 and 0.15 for the intensities ratios $L_1(\Gamma_7)/0(\Gamma_7)$ and $L_2(\Gamma_7)/0(\Gamma_7)$. The very weak features noted by arrows in Fig. 1 are attributed to the $^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$ surrounding. The relative intensities of the Si combinations scale with the fourth powers of the Si isotopic abundances and this is consistent with the existence of four equivalent Si atoms surrounding the S atom. The results obtained for S^+ are summarised in Table 1.

We have looked for similar isotope effects for the $1s(T_2)$ doublet of Se^+ in silicon [4]. The profile of $\Gamma_7(Se^+)$ is shown in Fig. 2. The low-energy side of $\Gamma_7(Se^+)$ is about two times broader than the high-energy side and no structure is observed but a shoulder, noted by an arrow in Fig. 2. The Se isotopes are ^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , ^{80}Se and ^{82}Se with natural abundances of 0.009, 0.094, 0.076, 0.238, 0.496 and 0.087, respectively. We have assumed that the ISs for Se^+ had the same signs as those for S^+ and they are adjusted to fit the experimental profile. In addition to the most intense components, the contributions of $^{74}\text{Se}^{28}\text{Si}_4$, $^{78}\text{Se}^{28}\text{Si}_3^{29}\text{Si}^{30}\text{Si}$ and $^{80}\text{Se}^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$ have also been

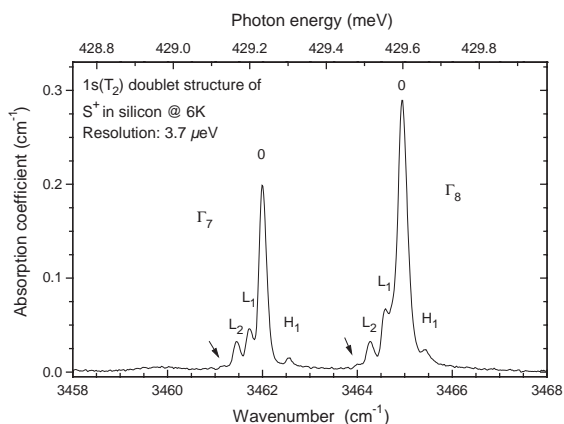


Fig. 1. Fine structure of the Γ_7 – Γ_8 doublet of $1s(T_2)$ of S^+ . The full widths at half maximum (FWHM) of $0(\Gamma_7)$ and $0(\Gamma_8)$ are 22 and 30 μeV , respectively, and their separation 0.365(4) meV.

Table 1
Shifts (μeV) from the 0 lines of the $1s(T_2)$ isotope satellites of S^+ (accuracy $\pm 7\mu\text{eV}$)

Satellite	$1s(T_2)\Gamma_7$	$1s(T_2)\Gamma_8$	Attribution
H_1	+69	+59	$^{34}\text{S}^{28}\text{Si}_4$
	+35		$^{33}\text{S}^{28}\text{Si}_4$
0	–	–	$^{32}\text{S}^{28}\text{Si}_4$
L_1	–34	–44	$^{32}\text{S}^{28}\text{Si}_3^{29}\text{Si}$
L_2	–69	–84	$^{32}\text{S}^{28}\text{Si}_3^{30}\text{Si}$
	–100	–120	$^{32}\text{S}^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$

The positions of $0(\Gamma_7)$ and $0(\Gamma_8)$ are 429.233 and 429.599 meV, respectively. The value of $35\mu\text{eV}$ for the ^{33}S shift is obtained by linear interpolation with the ^{34}S value.

The last line gives an estimation of the positions of the components noted by arrows in Fig. 1.

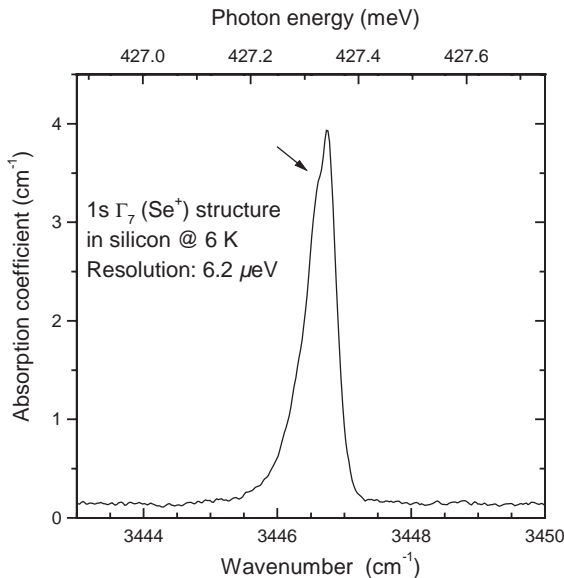


Fig. 2. Component Γ_7 of $1s(T_2)$ of Se^+ in Se-doped silicon with the same abscissa scale as in Fig. 1. The separation from component Γ_8 (not shown) is 2.27 meV. The FWHM of the structure is 61 μeV .

included. The best fit is shown in Fig. 3 and despite small differences due to the crudeness of the assumptions used, specially the one concerning fully symmetric components, the overall agreement with the observed profile favours the role of isotope effects in the $\Gamma_7(\text{Se}^+)$ line shape. This fit is obtained with a FWHM of 27 μeV , a Se isotope shift of +11 $\mu\text{eV}/\text{nucleon}$ and a Si isotope shift

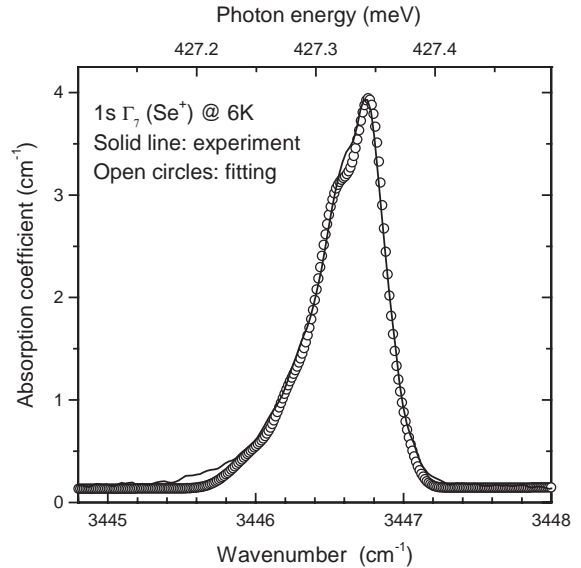


Fig. 3. Peak fitting of component Γ_7 of Se^+ to Si and Se isotope effects. The relative intensities of the 18 individual components considered for the fit are determined from the isotope relative abundances, the peak absorption of $^{80}\text{SeSi}_4$, taken as 3.28 cm^{-1} , and its energy, 3446.78 cm^{-1} (427.346 meV). Only one isotope shift is used for each element (see text).

of $-34\mu\text{eV}/\text{nucleon}$, close to the one for $\Gamma_7(\text{S}^+)$. Component $\Gamma_8(\text{Se}^+)$ has a FWHM near 250 μeV and it does not show the asymmetry of $\Gamma_7(\text{Se}^+)$, so that no isotope fitting has been tried on this component.

3. Discussion

Opposite ISs due to C and Si have already been reported for carbon-related complexes produced in silicon by electron irradiation [6]. We discuss the ISs reported here in the frame of a tetrahedral XSi_4 cluster (X is S or Se) model in the valence force approximation. In II–VI semiconductors, the radial force constant is much larger than the transverse one [7] and to simplify, we assume that this holds also for silicon. By neglecting the transverse mode, we consider only for the X^{28}Si_4 cluster the α_1 and τ_2 modes transforming, respectively, as the one- and three-dimensional representations Γ_1 and Γ_5 of T_d .

In a first step, we consider the vibronic coupling with the α_1 mode. In this case, the energy E of an optical transition has three contributions: (i) a purely electronic one, (ii) one involving lattice relaxation and (iii) one coming from the zero-point energies of both the ground and excited states. To the first order, the first two contributions cannot produce any isotope effect. For the $X^{28}\text{Si}_4$ cluster, the zero-point energy contribution to E is

$$\frac{\hbar}{2}[(\omega_1^e - \omega_1^g) + 3(\omega_5^e - \omega_5^g)], \quad (1)$$

where the index refers to the representations of the modes and the superscript to the excited (e) or ground (g) electronic state. When one ^{28}Si atom of the cluster is replaced by another isotope ^iSi , the symmetry of the cluster changes to C_{3v} and τ_2 splits into two modes with frequencies ω_{51} and ω_{53} , transforming like the Γ_1 and Γ_3 representations of C_{3v} (ω_1 changes to ω_{11}). The zero-point energy contribution of $X^{28}\text{Si}_3^i\text{Si}$ is thus

$$\frac{\hbar}{2}[(\omega_{11}^e - \omega_{11}^g) + (\omega_{51}^e - \omega_{51}^g) + 2(\omega_{53}^e - \omega_{53}^g)] \quad (2)$$

and the electronic Si IS δ_{Si} is the difference between expressions (2) and (1). If the frequencies of the modes are the same in the electronic ground and excited states, δ_{Si} is zero. One condition to observe an IS is the difference of electronic densities at the atom site in the ground and excited states [8]: an extra electric charge (electron or hole) localised in the vicinity of an atomic cluster softens the force constants between the atoms of the cluster. This results in a reduction of the frequencies of the modes of the cluster in the ground state, compared to the excited state where the electronic density is weaker. The above frequencies can be formally derived from [9]. Within the valence force approximation, $\omega_{11} = \omega_1 \sqrt{1 - \kappa}$, $\omega_5 = \omega_{53} = \omega_1 \sqrt{1 + A}$ and $\omega_{51} = \omega_1 \sqrt{1 + A - 3\kappa}$, where $\omega_1 = \sqrt{k/m}$ is the frequency of the α_1 mode. The quantities $\kappa = \Delta m/4(m + \Delta m)$ and $A = 4m/3M_X$ are expressed in terms of the mass M_X of atom X and of the masses m and $m + \Delta m$ of the ^{28}Si and ^iSi atoms. The IS δ_{Si} thus reads:

$$\delta_{\text{Si}} = \frac{\hbar}{2}[(\omega_{11}^e - \omega_1^e) - (\omega_{11}^g - \omega_1^g) + (\omega_{51}^e - \omega_5^e) - (\omega_{51}^g - \omega_5^g)] \quad (3)$$

For an electron bound to a donor, the more localized the electron, the weaker the force constant: the X-Si spring constant k is then smaller in the ground state (k_g) than in the excited state (k_e). For $\kappa \ll 1$, the explicit form for δ_{Si} is

$$\delta_{\text{Si}} = -\frac{\hbar\omega_1^e}{4}\kappa \left[1 + \frac{3}{\sqrt{1+A}} \right] \left(1 - \sqrt{\frac{k_g}{k_e}} \right). \quad (4)$$

Expression (4) is negative, as observed. In order to evaluate the bond softening, an estimation of ω_1 is required. A resonance ascribed to P^+ has been reported in silicon [10] at 55 meV ($\approx 445 \text{ cm}^{-1}$). Besides the nuclear charge, the mass and electronic structure of S^+ are close to those of P^+ so that a mode frequency of 500 cm^{-1} seems to be a right order of magnitude for ω_1 . In order to match the experimental value of the $^{32}\text{S}^{28}\text{Si}_4$ - $^{32}\text{S}^{28}\text{Si}_3^{29}\text{Si}$ IS ($-34 \mu\text{eV}$) for the transition towards the $1s(\text{T}_2)\Gamma_7$ level of S^+ , the ratio k_g/k_e deduced from expression (4) must be ≈ 0.84 .

The same mode softening is responsible for an IS when $^{32}\text{S}^{28}\text{Si}_4$ is replaced by $^{34}\text{S}^{28}\text{Si}_4$, and this shift is predicted to be negative. The observed positive S IS implies that it must include another mechanism.

One important point has been omitted in the above description of the S IS, namely the electron- τ_2 local mode coupling. If it has no effect on the ground state orbital singlet, it modifies the excited states, which originate from an orbital triplet, through a $\text{T}_2 \otimes \tau_2$ vibronic coupling. The electron-local mode coupling is a purely electronic term and the Jahn–Teller energy E_{JT} is therefore independent of the mass of the chalcogen. It can be written $E_{\text{JT}} = V_{\text{T}}^2/3\mu\omega_5^2$ where V_{T} is the coupling constant and μ the reduced mass of the τ_2 mode. The term $\mu\omega_5^2$ is simply the mass-independent spring constant. The energy of the lower vibronic excited state [11] becomes $E_{\text{el}} - E_{\text{JT}} + \gamma\hbar\omega_5^e$. The two first terms of this expression are independent of the mass of the chalcogen atom and γ is a factor that can take values between 1.2 and 3/2 [11]. When the zero-point energy in the excited state $3\hbar\omega_5^e/5$ is replaced by $\gamma\hbar\omega_5^e$, the expression for δ_{S} is

$$\delta_{\text{S}} \approx \hbar\omega_1^e [\sqrt{1 + \Lambda_{34}} - \sqrt{1 + \Lambda_{32}}] \left(\gamma - \frac{3}{2} \sqrt{\frac{k_g}{k_e}} \right). \quad (5)$$

For $\gamma < 3/2\sqrt{k_g/k_e}$, the IS δ_S is positive, as observed. With the above value of k_g/k_e , γ must be less than 1.374. This corresponds to a value of $\sqrt{3E_{JT}/2\hbar\omega_S^e}$ larger than 0.7 and this means that for a rather moderate strength of the $T_2 \otimes \tau_2$ vibronic coupling, the chalcogen IS becomes positive. To reproduce the observed value of δ_S , γ must be 1.327, which corresponds to $E_{JT}/\hbar\omega_S^e = 1.1$.

4. Conclusion

We have produced evidence of two opposite ISs of lines of the spectrum of S^+ in silicon and we have shown that they can explain the profile of one of the corresponding lines of Se^+ in silicon. The negative Si shift can be explained by a softening of the chalcogen-Si bonds in the ground state due to the localisation of the donor electron. The positive chalcogen IS can be understood in terms of a vibronic coupling of the excited electronic triplet state with the triply degenerate local vibrational mode involving a displacement of the chalcogen atom. This effect combined with the bond softening is shown to be able to produce a positive S IS.

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