

A spectroscopic investigation of the lattice distortion at substitutional sites for groups V and VI donors in silicon

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Abstract. Differences between experimentally determined line spacings in the spectra of group V donors in silicon and the corresponding spacings from an effective-mass-theory model supply information on the local volume change produced when a group V atom replaces a silicon atom. The results show that the volume change is negative for phosphorus and positive for the other donors. For group VI neutral donor spectra, the same figures are found for S⁰ and Se⁰, as compared with P and As, respectively. This similarity is considered as experimental proof that isolated sulphur and selenium occupy substitutional sites in silicon. A spectroscopical argument is put forward that shows that if sulphur and selenium are substitutional, then tellurium must also be substitutional and the problems encountered in trying to obtain information on the structure of the chalcogen complexes by this technique are briefly discussed. The information obtained spectroscopically on the lattice distortion at the donor site are compared with recent calculations and with other experimental results.

1. Introduction

Infrared (IR) studies of shallow impurities in silicon and germanium have been used mostly as a characterisation technique and as a method to provide accurate values of the ground-state binding energies of the centres investigated (Ramdas and Rodriguez 1981). One of their other merits is to have elevated the spectroscopy of semiconductors into a branch of spectroscopy in its own right, that closely parallels atomic spectroscopy. Information on the band structure of the host lattice, which can necessitate the use of external perturbations such as uniaxial stresses or magnetic fields, has also been obtained by IR spectroscopy, but contrary to EPR, and for quite understandable physical reasons, not much has been learned of the atomic structure of the centres nor of the perturbation of the lattice in their immediate vicinity using IR spectroscopy.

In this paper, however, we present very simple spectroscopical data that are analysed to measure the local change in the volume of the lattice when a group V donor replaces a silicon atom in the lattice. Previous results and similar data are used to give clear experimental evidence that isolated chalcogens enter the silicon lattice substitutionally and not interstitially.

2. Features of the single-donor spectra in silicon

The discrete IR absorption of group V donors in silicon consists mainly of parity-allowed transitions of the donor electron arising from the $1s$ ground state to the np , nf and nh states. These excited states are each split by the anisotropy of the electron effective mass, which also lifts the degeneracy between the different values of m of the projection of the l quantum number on an anisotropy axis. So, a level with $n = 3$ and $l = 1$ ($3p$ level) is split into a $3p_{m=0}$ and a $3p_{m=\pm 1}$ level and two corresponding IR lines labelled $3p_0$ and $3p_{\pm}$ are observed.

The electronic degeneracy of an electron bound to a single donor in silicon is assumed to be the same as that of a free electron, i.e. a sixfold degeneracy along a $\langle 100 \rangle$ direction in k space as well as in ordinary space. This degeneracy is lifted for the electron bound in the ns states by the so called 'chemical splitting' or 'valley-orbit splitting' into three sublevels, $ns(A_1)$, $ns(E)$ and $ns(T_2)$ where A_1 , E and T_2 label irreducible representations of the tetrahedral group (Kohn and Luttinger 1955). For all group V donors, the ground state is the $1s(A_1)$ level and its binding energy varies from 42.8 meV for antimony to 71.0 meV for bismuth. The energies of the $1s(E)$ and $1s(T_2)$ levels are not affected so much by the chemical nature of the impurity and their binding energies are about 32 meV. The chemical shift for the ns levels decreases with increasing n and it is negligible for $n = 6$. The np_0 and np_{\pm} levels are similarly degenerate ($(A_1 + E + T_2)$ for np_0 and $2(T_1 + T_2)$ for np_{\pm} levels) but, contrary to the ns states, the symmetry of the 'atomic' wavefunctions precludes the lifting of the degeneracy. In addition to the parity-allowed IR transitions, some parity-forbidden, symmetry-allowed transitions from the ground state to the $ns(T_2)$ and $3d_0$ states are also observed (Kleiner and Krag 1970). The order of magnitude of the smallest linewidths found in the spectra of donors in silicon below 10 K is 0.2 cm^{-1} or $25 \text{ } \mu\text{eV}$ (Jagannath *et al* 1979, Pajot *et al* 1979, 1985).

3. The effective-mass model and the lattice perturbation

The one-valley Hamiltonian of an electron with an anisotropic effective mass bound to an immobile positive charge reads, when expressed in scaled atomic units (Faulkner 1969)

$$H_0 = \nabla^2 + (1 + \gamma) \partial^2 / \partial z^2 - 2/r \quad (1)$$

where γ is the ratio of the transverse and longitudinal effective masses of the conduction electron. The eigenvalues of H_0 can readily be derived but they are not correct solutions for the energy levels as H_0 also has non-zero, non-diagonal elements with respect to the whole set of 'atomic' wavefunctions of given parity. One method of calculation consists of a variational determination of the whole set of eigenvalues of a matrix made from a sufficiently extended set of 'atomic' wavefunctions (Faulkner 1969, Janzén *et al* 1984, Bara *et al* 1985). Another method based on the reduced-matrix-element technique has also been used recently to obtain the donor energy levels (Broeckx *et al* 1986); this presents a definite advantage over the former method, due to the choice of a different representation that eliminates non-linear parameters from the radial functions. For the sake of completeness, let us also mention the work of Kogan and Taskinboev (1983) who use a *non-variational* method to calculate the excited donor levels in silicon and germanium.

Comparison of the eigenvalue differences with the differences between the lines observed shows that the energies of the odd-parity levels can be calculated with good accuracy in the one-valley approximation, although some deviations can be discerned for highly excited levels (Pajot *et al* 1985). For some time, experimental and computational accuracies were such that any difference between the two sets of values could not be discussed significantly. Recently, however, two independent variational calculations using slightly different minimisation criteria have provided computed values of the first np and nf levels that agree to within $\pm 3 \times 10^{-3}$. On the experimental side, high-resolution, high-sensitivity Fourier transform IR spectroscopy of groups V and VI in silicon (Pajot *et al* 1979, 1985, Pajot 1984, Pajot and Naud 1984) has yielded accurate values of the line positions and their spacings. In such a situation, any chemical trend other than the ground-state 'chemical' effect could be analysed to obtain information on the local interaction between the dopant atom and the host lattice. It was also possible to compare the situation for each group V donor and its group VI neighbour in the Periodic Table in order to derive information on the donor chalcogen complexes in silicon from the spectroscopical data.

The one-valley Hamiltonian (equation (1)) is assumed to describe the situation where an immobile positive electron charge and a conduction electron interact through a Coulomb potential screened by the static dielectric constant of the crystal. The positive charge is supposed to leave the lattice undisturbed, but physically this cannot be the case when a donor atom replaces an atom of the crystal because, for instance, of the differences in atomic radii. The question of the changes in the eigenvalues of (1) induced by the lattice deformation arising from the introduction of the donor atom has been addressed by Stoneham (1975). The basis of the method is to derive the perturbation $V(r)$ induced by the foreign atom as a function of the conduction-band deformation potentials Ξ_v and Ξ_d (assumed to be the same as those for weakly bound electrons; this is totally justified in the present case (Belyaev *et al* 1986)) and of the actual strain near the donor site. $V(r)$ is treated as a perturbation term in (1) and the resulting diagonal term can be computed for different effective-mass levels as a function of the actual strains at the impurity site. The shift of the levels can then be related to the relative macroscopic volume change due to the donor when it has replaced an atom of the crystal (Stoneham 1975). In outline, one needs to estimate the strain field in terms of the volume change ΔV and to isolate the components that contribute to the perturbation $V(r)$. It is assumed that the short-range 'ionic radius' defect forces are predominant, i.e. that the donor electron itself monitors the strain field but does not cause any significant distortion. This is supported (Stoneham 1979) by the analysis of highly doped laser-annealed Si:B. There prove to be two key contributions to $V(r)$. The larger term comes from the elastic anisotropy and (to a lesser extent) because the defect forces are not applied at a point in the continuum but at the neighbouring atoms to the impurity. A smaller contribution comes from the conduction band anisotropy. In this approach, elasticity theory and deformation potentials are clearly used closer than usual to their limits of validity, so caution should be exercised concerning precise values of the volume change. The results can be obtained by numerical integration and expressed in terms of a small number of constants, these involving host-lattice properties (i.e. the deformation potential, elastic constants and effective-mass Bohr radii for the donor electron), a cut-off c to describe the short-range variation of the strain and the volume change ΔV for the donor in a large finite crystal. Every energy level should be shifted by this perturbation, but the deeper the level the stronger the shift. To see if such shifts can be detected in practice, one must compare the experimental splitting between two lines with the calculated splitting

Table 1. Comparison between the $3p_{\pm} - 2p_{\pm}$, $2p_{\pm} - 2p_0$ or S_{2p} and $3p_{\pm} - 3p_0$ or S_{3p} spacings (cm^{-1}) for group V donors in silicon compared with the point-charge model. The effective Rydberg is taken as 161.19 cm^{-1} (19.988 meV). In parentheses are given the dimensionless spacings $S_{2p \text{ or } 3p} / (3p_{\pm} - 2p_{\pm})$.

Spacing	EMT	P	As	Sb	Bi
$3p_{\pm} - 2p_{\pm}$	26.47	26.47 ± 0.04	26.44 ± 0.10	26.32 ± 0.20	26.33 ± 0.10
S_{2p}	41.08 (1.552)	40.86 ± 0.04 (1.544 \pm 0.004)	41.15 ± 0.10 (1.556 \pm 0.010)	41.38 ± 0.20 (1.57 \pm 0.02)	—
S_{3p}	19.10 (0.722)	19.00 ± 0.04 (0.718 \pm 0.003)	19.06 ± 0.10 (0.721 \pm 0.007)	19.09 ± 0.20 (0.725 \pm 0.013)	19.23 ± 0.10 (0.730 \pm 0.007)

between the corresponding excited levels without including the perturbation term. Any systematic trend would indicate the detectability of the effect. If the effect can be observed, it can then be used to evaluate the local displacement and the macroscopic change in volume associated with the introduction of the isolated donor impurity in the crystal.

4. Interpretation of the group V donor differences

Table 1 gives a comparison of the observed separations between the first-excited levels of the group V donors in silicon (Pajot *et al* 1979) with the calculated ones. Note that the accuracy on the spacings is better than that on the absolute position of the individual lines. The $2p_0$ line of bismuth at 480 cm^{-1} interacts resonantly with optical phonons of the silicon lattice (Onton *et al* 1967) so that its spacing with the $2p_{\pm}$ line is not meaningful; it was hence discarded. Inconsistencies were found for the Sb line positions reported due to the low transmission of the sample for the $2p_{\pm}$ line, and the spacings have been re-measured directly on the spectra. The calculated reduced spacings are the ratio of the spacings expressed in scaled atomic units and the effective Rydberg is calculated so as to match the $3p_{\pm} - 2p_{\pm}$ spacing of phosphorus.

The first row of table 1 shows that the $3p_{\pm} - 2p_{\pm}$ spacings display a small decrease (0.14 cm^{-1} or $17 \mu\text{eV}$) when going from phosphorus to bismuth. More interesting are the S_{2p} and S_{3p} spacings, which do exhibit a definite donor-dependent trend. It could be argued that, despite the fact that the wavefunctions involved have a node at the central site, what is actually observed is a 'chemical' effect experienced by the excited levels of the same physical origin as that felt by the $1s(A_1)$ ground state. If this were the case, the same trend could be expected in the differences observed for the excited levels as in the binding energy differences of the ground state, i.e. the smallest effect would be observed for antimony, which shows the smallest 'chemical' effect of all group V donors, but this is not consistent with observation.

The donor-dependent differences between the one-valley effective-mass-theory (EMT) results and the experimental data can be interpreted in the framework of the lattice distortion model as the addition to the EMT value of a donor-dependent perturbation, that is the quantity measured experimentally. The order of magnitude of the relative volume change $\Delta V/V_0$, where V_0 is the volume of a silicon atom and ΔV is the volume change

Table 2. Same spacings (cm^{-1}) as in table 1 for isolated group VI neutral donors and interstitial lithium in silicon, with addition of the $5p_{\pm} - 3p_{\pm}$ spacing.

Spacing	EMT	S ⁰	Se ⁰	Te ⁰	Li _(i) ^a
$3p_{\pm} - 2p_{\pm}$	26.47	26.47 ± 0.01	26.46 ± 0.01	26.37 ± 0.04	26.5
S_{2p}	41.08 (1.552)	40.86 ± 0.01 (1.544 \pm 0.001)	41.15 ± 0.01 (1.555 \pm 0.001)	41.70 ± 0.04 (1.58 \pm 0.04)	41.2
S_{3p}	19.10 (0.722)	18.95 ± 0.05 (0.716 \pm 0.004)	19.08 ± 0.02 (0.721 \pm 0.002)	19.24 ± 0.04 (0.730 \pm 0.004)	19.1
$5p_{\pm} - 3p_{\pm}$	13.48	13.36 ± 0.05 [P: 13.39 \pm 0.04]	13.42 ± 0.03 [As: 13.38 \pm 0.10]	13.37 ± 0.05	

^a Ramdas and Rodriguez (1981).

produced by its substitution by a group V donor, D (Stoneham 1975) is:

$$\Delta V/V_0 = 2.9(\text{meV})^{-1}(S_{2p}(\text{D}) - S_{2p}(\text{EMT})) (\text{meV}). \quad (2)$$

In this expression, some uncertainty comes from the determination of the effective Rydberg needed to express $S_{2p}(\text{EMT})$ in spectroscopic units. Usually, the $2p_{\pm} - 3p_{\pm}$ spacing for P is put equal to the $2p_{\pm} - 3p_{\pm}$ EMT spacing in spectroscopic units, but it is also true that the value of $S_{2p}(\text{EMT})$ is critical for the comparison. It is preferable to use for the determination of $\Delta V/V_0$ the dimensionless spacings S'_{2p} given in parentheses in tables 1 and 2: the difference $S'_{2p}(\text{D}) - S'_{2p}(\text{EMT})$ is then between an experimental value and a purely calculated one, 1.552. The scaling appears only in the factor $(2p_{\pm} - 3p_{\pm})$ of this difference, where the knowledge of its exact value is not so crucial.

Using the $2p_{\pm} - 3p_{\pm}$ spacing for P, 3.282 meV,

$$\Delta V/V_0 = 9.52(S'_{2p} - 1.552). \quad (3)$$

For phosphorus, the difference is negative and it amounts to -0.008 ; it corresponds to a spectroscopic difference of $26 \mu\text{eV}$ or 0.21 cm^{-1} . This implies a contraction of the lattice when phosphorus replaces silicon in the crystal and a spectroscopic value of -0.08 is obtained for the relative volume change. Similarly, for arsenic and antimony, $\Delta V/V_0$ deduced from table 1 are $+0.04$ and $+0.17$, respectively.

5. Interpretation of group VI donor differences

Many of the chalcogen-related centres, including the isolated atoms, are double donors (Wagner *et al* 1984), and their neutral-charge state is a solid state analogue of neutral helium. Compared with group V substitutional donors, the extra electron can explain the double-donor properties of the isolated atom, also assumed to be on a substitutional site. There are, however, slight doubts about this interpretation, raised by (i) the relatively high diffusion coefficients of chalcogens in silicon, and (ii) ENDOR results that can be interpreted assuming an interstitial site as well as a substitutional site (Niklas and Spaeth 1983).

The spectra of isolated neutral chalcogens in silicon are well identified (Janzén *et al* 1984, Wagner *et al* 1984). High-resolution spectra of isolated neutral chalcogens and of chalcogen complexes have been obtained using a Bomem DA3-01 Fourier transform

spectrometer (Pajot 1984, Pajot *et al* 1985). The spacings between the first-excited levels of the isolated neutral chalcogens in silicon are given in table 2. The last row of this table shows that the $5p_{\pm} - 3p_{\pm}$ spacings for the three chalcogens, phosphorus and arsenic are independent of the donor and that the $3p_{\pm}$ level should be chosen when possible as the origin of the donor-dependent shifts. Comparison of table 2 with table 1 reveals the close similarity of the spacings for P and S^0 on the one hand and those for As and Se^0 on the other hand (Bara *et al* 1985). Such a similarity can be understood if sulphur and selenium occupy the same substitutional sites as phosphorus and arsenic. The case for tellurium is not so evident as the comparison with antimony does not show the expected correlation, but this could be due to the poor accuracy of the antimony spectroscopical data.

This similarity in the $2p_{\pm} - 2p_0$ (S_{2p}) spacing provides experimental confirmation that isolated S and Se atoms enter substitutionally in the silicon lattice. Such conclusions had already been reached theoretically from comparisons of total energy calculations (Beeler *et al* 1985). These calculations showed that the incorporation in the silicon lattice of substitutional chalcogens is energetically favoured (exothermal) over the incorporation on an interstitial site and that the stability increases from sulphur to tellurium.

Experimentally, similarities between the IR spectra of the three isolated chalcogens can be considered as evidence that, if isolated sulphur and selenium are substitutional—and this we have shown to be the case—then tellurium must also be substitutional in the silicon lattice. The main similarity is the observation for the three chalcogens of $1s(A_1) \rightarrow ns(T_2)$ parity-forbidden, symmetry-allowed transitions. In sulphur and tellurium, they can be followed up to $3s(T_2)$ and up to $4s(T_2)$ in selenium. These relaxations of the selection rules arise from the mixing of p-like components in the components of the $ns(T_2)$ multi-valley wavefunction. This mixing increases with the ionisation energy of the donor atom, but it is also determined by the shape of the impurity potential in the vicinity of the nearest neighbours: whereas the $1s(A_1) \rightarrow 1s(T_2)$ transition, split by a spin-orbit interaction, is observed for the group V donor bismuth with $E_i = 71$ meV (Krag *et al* 1970), it has not been observed for the interstitial double donor neutral magnesium with $E_i = 107.5$ meV (Ho and Ramdas 1972, Kleverman *et al* 1986). This is to say that if tellurium were interstitial, the $1s(A_1) \rightarrow 1s(T_2)$ transition, if detected, should be much weaker than it is actually observed to be. So we can conclude that isolated tellurium in silicon also occupies a substitutional site. Figure 1 gives a plot of S_{2p} against S_{3p} for the groups V and VI donors investigated in the present study. To be fair, the accuracy of the measurement for As and Sb is such that the actual value of the slope of the line for the group V donors is probably not significant, but for the group VI donors the empirical relationship $S_{3p}(\text{cm}^{-1}) = 0.3 \times S_{2p}(\text{cm}^{-1}) + 6.72(\text{cm}^{-1})$ provides a good fit of the experimental S_{3p} values once S_{2p} is known; this relationship also holds for the P and As spacings which are more accurate than those for Sb. From the experimental S_{3p} spacing for Bi, we can deduce a 'resonance-free' S_{2p} spacing that provides an extrapolated value of +0.30 for the relative volume change when this atom replaces a silicon atom.

In table 2 we include the spacings for isolated interstitial lithium (Ramdas and Rodriguez 1981) that provide $S'_{2p} = 1.56$. It is clear that the accuracy for Li_i could be better if the position of the lines were indicated instead of the energy of the levels. A direct measurement of the spacings on the expanded high-resolution spectrum of Li_i and Li-O (Jagannath and Ramdas 1980) yields $S'_{2p} = 1.567$. This seems to show that the introduction in the silicon lattice of a small interstitial atom does produce some deviation from the calculated EMT spacing. The point is that for a bigger interstitial atom such as

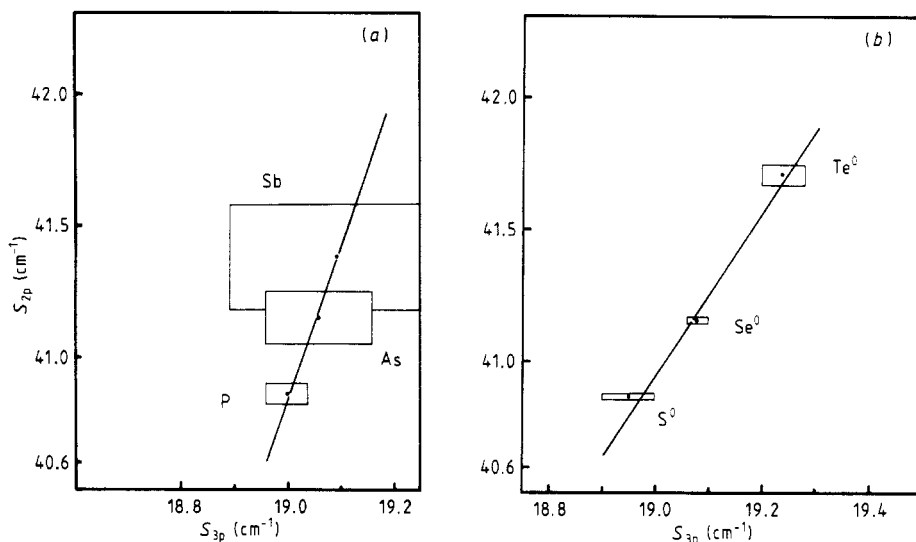


Figure 1. Experimentally determined spacings (cm⁻¹) $2p_{\pm} - 2p_0$ (S_{2p}) against $3p_{\pm} - 3p_0$ (S_{3p}) (a) for different group V donors and (b) for group VI neutral donors in silicon fitted against a linear dependence. The approximate relationship $S_{3p} \approx 0.3S_{2p} + 6.72$ seems to hold for the spectra of the chalcogens and chalcogen-related complexes.

magnesium S_{2p} reaches 42.9 cm⁻¹, indicating that when the size of the interstitial atom increases, the magnitude of the distortion increases too.

6. Comparison with other results

The spectroscopical volume changes obtained here are definitely smaller than the simple estimations derived from a comparison of the Pauling's tetrahedral covalent atomic radii of the atoms (Kittel 1968), in which ΔV is the difference between $V_0(\text{Si})$ and V for the donor atoms. These values of $\Delta V/V_0$ are: -0.17 (Si:P), $+0.03$ (Si:As) and $+0.57$ (Si:Sb), but the qualitative agreement seems to confirm the validity of the model used and it suggests that the forced hybridisation of the atomic orbitals could be the origin of the apparent shrinking of the free atom when tetrahedrally bound in the silicon lattice. An overall negative volume change due to phosphorus diffusion in silicon has been reported previously: -0.11 by Cohen (1967) and -0.15 by McQuhae and Brown (1972), but recent x-ray measurements of the Si lattice expansion indicate a small increase of the lattice parameter when phosphorus is introduced in low concentration (Becker and Scheffler 1984).

The local relative volume changes for group V donors and neutral group VI donors in silicon, deduced from the spectroscopical data using equation (3), are summarised in table 3 and they are compared with Pauling's tetrahedral radii. The table shows that if we correlate these radii to the spectroscopical volume changes, we should observe a higher contraction for S⁰ than for P, a small contraction for Se⁰ and for Te⁰ an expansion comparable to that for Sb. In our opinion this shows the limits of the use of these radii for predicting local lattice changes. It may be that trends can also be predicted by simple methods like Baranowski's (1984) which look at the systematics of the local distortions in terms of specified covalent and overlap interactions.

Table 3. Low-temperature relative local volume changes $\Delta V/V_0$ determined spectroscopically for group V donors and group VI neutral donors in silicon. The Pauling's empirical tetravalent radii and those of Van Vechten and Phillips (1970) are given for comparison. The tetravalent radius for Si is taken as 1.17 Å.

	P	As	Sb	Bi	S ⁰	Se ⁰	Te ⁰
$\Delta V/V_0$	-0.08	+0.04	+0.17	+0.30 ^a	-0.08	+0.03	+0.27
$a(\text{Å})^b$	1.10	1.18	1.36		1.04	1.14	1.32
$a(\text{Å})^c$	1.13	1.23	1.41		1.13	1.23	1.41

^a Extrapolated.

^b Pauling's values.

^c Van Vechten and Phillips (1970).

Calculations of the equilibrium coordinates of the first-nearest neighbours of P⁺, As⁺, S⁰, S⁺ and S⁺⁺ in silicon have been performed using the density functional theory within the local-density approximation (Scheffler 1986). For the shallow group V donors, the weakly bound electron is ignored as it is assumed that the charge density at the donor site and in its immediate vicinity is nearly the same, whether the donor is ionised or not. This assumption can no longer be justified for S⁰ and S⁺ with ionisation energies of 0.32 and 0.61 eV, respectively, and the relaxation near this atom is calculated for the three possible charge states. The results of these calculations, expressed in relative units u/d_0 (u is the displacement of the nearest neighbour and d_0 is the normal Si-Si distance of 2.346 Å), predict a small inwards distortion (between 0 and -0.009) for P⁺ while for As⁺ it is between +0.009 and +0.021. This does not contradict the spectroscopical results. For S⁰, however, these calculations indicate an outwards distortion of +0.021 while our data predict for S⁰ the same inwards distortion as for P.

An estimate of the lattice distortion for S⁺ has also been deduced by Scheffler (1986) from the EPR measurements of Ludwig (1965): it shows a very small inward distortion compared with the calculated value of +0.009.

Direct measurements of ΔV from the changes in the lattice parameters with concentration are practical only at rather high concentrations, typically in excess of a few $\times 10^{18}$ atoms cm⁻³. Moreover, these also show an initial dependence on concentration that goes over to a different linear dependence at concentrations approaching 10¹⁹ atoms cm⁻³ and above (Becker and Scheffler 1984). In this high-concentration regime, the data can be described as $\Delta V/V_0 = -0.01$ (Si:B, -0.2 (Si:P), -0.01 (Si:As) and

Table 4. Same spacings (cm⁻¹) as in table 1 for some of the first neutral chalcogen-related centres in silicon with their optical ionisation energy (E_i). The isolated atoms have been included to show the trends.

Spacing	S ⁰	S ₂ ⁰	S _c ⁰ (X ₁)	Se ⁰	Se ₂ ⁰	Te ⁰	Te ₂ ⁰	Te _c ⁰ (X ₁)
3p _z - 2p _z	26.47	26.48 ^a	26.41 ^b	26.46	26.39	26.37	26.1	26.2
S _{2p}	40.86	41.15 ^a	41.84 ^b	41.15	41.68	41.70	42.4	44.1
S _{3p}	18.95	19.04 ^a	19.27 ^b	19.07	19.21	19.24		
E_i (meV)	318.38	187.66	109.55	306.71	206.50	198.91	158.18	127.0

^a Uncertainty ± 0.01 cm⁻¹.

^b Average: the S_c⁰(X₁) lines have a complex structure.

+0.42 (Si:Sb). The same trend can be seen in our spectroscopic results, but there are many possible reasons for the differences.

Extended x-ray-absorption fine structure (EXAFS) measurements, however, give directly the closest interatomic distances. In isotropic elasticity, the displacements have the form Du/r^2 , where $D = [\Delta V(c_{11} + 2c_{12})/12\pi c_{11}]$. The results of Erbil *et al* (1986) for Si:As give an 0.06 Å outward motion of the nearest neighbours (hence $\Delta V/V_0 \approx 0.51$ with isotropic elasticity). The combination of EXAFS with our spectroscopical approach should define the strain field of single donors rather well. However, one should not underestimate the problems of relating ΔV to the nearest-neighbour displacements, even in simple cases (Bass *et al* 1984).

7. The differences for some neutral chalcogen complexes

The trend in the line spacings when going from the isolated substitutional chalcogens to other chalcogen-related centres is summarised in table 4 for the first neutral centres. If compared with the spacings for the isolated atoms, it is seen that the overall effect when going from isolated sulphur or selenium to the corresponding pairs is about the same as when going from isolated sulphur to isolated selenium or from isolated selenium to isolated tellurium. As far as we can speak of a global effect near a substitutional site, this change agrees with an increase of the size and mass of the centre. The point is that the chalcogen pairs can no longer be considered as substitutional centres.

The point group symmetry of the chalcogen pairs was first established to be C_{3v} by Ludwig (1965). More recently, group-theoretical arguments based on spectroscopical results have been given by Janzén *et al* (1984) which seem to show that the symmetry of the chalcogen pairs is D_{3d} rather than C_{3v} . This implies that the pair is symmetrical with respect to an inversion centre, so that the two chalcogen atoms must be located on equivalent sites. From the theoretical side, the nearest-neighbour substitutional pair seems to emerge from the substitutional cluster model developed by Jansen and Sankey (1986) and also from the density functional calculations by Weinert and Scheffler (1986). The latter calculation, however, is not adequate to treat the thermodynamic stability of the substitutional–interstitial pair. The spectroscopy of silicon samples co-doped with two different chalcogens has shown that mixed chalcogen pairs (e.g. S–Se) could indeed be formed which must display C_{3v} symmetry, but no drastic difference with the assumed D_{3d} symmetry of the pairs made up from two identical atoms was observed (Wagner *et al* 1984).

From the negative change of $\Delta V/V_0$ for isolated sulphur, we would also expect a local contraction of the lattice for the substitutional pair and this should not result in an increase of the S_{2p} spacing for S_2^0 relative to S^0 , as long as the lattice deformation in the vicinity of the centres is the only contribution to the change in the S_{2p} spacing. So the relative effect observed for S_2^0 , Se_2^0 and Te_2^0 would slightly favour a substitutional–interstitial model. Moreover, it has been shown above that an interstitial atom such as magnesium could produce a noticeable increase of S_{2p} and a similar effect could be expected from the interstitial sulphur atom of the pair.

We have applied the empirical relation obtained between S_{2p} and S_{3p} for isolated group VI donors to the same quantities derived from the chalcogen complex spectra, given in table 4. The relation is seen to yield the right order of magnitude, implying that the shift observed is related only to the lattice distortion, a point which validates our interpretation (table 5).

Table 5. Correlation between the observed S_{2p} and S_{3p} spacings (cm^{-1}) for various single and double donors in silicon. The $S_{3p}(\text{lin})$ spacings in the final column are obtained from: $S_{3p}(\text{lin}) = 0.3 \times S_{2p}(\text{exp}) + 6.72(\text{cm}^{-1})$.

Donor	$S_{2p}(\text{exp})$	$S_{3p}(\text{exp})$	$S_{3p}(\text{lin})$
P	40.86	19.00	18.98
As	41.15	19.06	19.07
S^0	40.86	18.95	18.98
Se^0	41.15	19.07	19.07
Te^0	41.70	19.24	19.23
S_2^0	41.15	19.04	19.07
Se_2^0	41.68	19.21	19.22
TDA ^{0a}	46.0 ± 0.1^b	20.4 ± 0.1^b	20.5

^a TDA⁰ is the deepest 'thermal' donor in silicon.

^b Pajot (1984).

8. Conclusion

The comparison of the spacings between calculated excited donor levels in silicon with the spacings of the corresponding IR absorption lines for the different group V donors has shown a trend with the chemical nature of the donor. This donor-related effect is detected for the $2p_0$, $2p_{\pm}$ and $3p_0$ levels using the $3p_{\pm}$ level as a reference. It has been related to the local relative volume change of the donor compared with the silicon atom it replaces. It is found that for phosphorus, the change in volume is negative while it becomes positive and increases steadily for the other donor atoms. A straightforward conclusion would be that for Si:P, the lattice should be in expansion whereas it should be in compression for the other group V donors. The main characteristics of these spectroscopically determined volume changes is that they are local, low-temperature (<10 K) changes measured for relatively low donor concentrations (less than 1 ppm). If several donors are present in the crystal, they will exhibit different spectral volume changes, but the overall change of the lattice parameter will be due to the contribution of all the different centres and defects present in the crystal. In addition to information on the relaxation of the silicon lattice near a donor atom, a knowledge of the donor-induced distortion experienced by the crystal can be useful for corrections on high-accuracy measurements of the silicon lattice spacing needed for a re-determination of the Avogadro constant (Siegert *et al* 1984).

The IR spectra of isolated sulphur and selenium, that immediately follow phosphorus and arsenic in the periodic table, present quantitatively the same differences as phosphorus and arsenic, respectively. This is strong experimental evidence that isolated sulphur and selenium enter substitutionally in the silicon lattice.

The recent calculations by Broeckx *et al* (1986) have provided more reliable values of the donor levels in germanium than those of Faulkner (1969). The estimation of the relative volume change for substitutional donors in germanium (Stoneham 1975) is $\approx 9.1(\text{meV})^{-1}(S_{2p}(\text{D}) - S_{2p}(\text{EMT})) \text{meV}$. Despite the fact that the calculated and experimental results are not given with the same accuracy as for donors in silicon, they show, however, that when isochoric antimony replaces a germanium atom, a negative volume change (≈ -0.2) occurs as in the case when isochoric phosphorus replaces a silicon atom

(table 3). This shows the need for highly accurate experimental and calculated values for donors in germanium.

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