

Electronic Structure of Platinum in Silicon

C. A. J. Ammerlaan and A. B. van Oosten

Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Received April 6, 1988; accepted June 22, 1988

Abstract

The negatively charged state of substitutional platinum in silicon is observable by electron paramagnetic resonance (EPR). The g -tensor of the EPR spectrum (labelled Si-Pt(I)) reveals orthorhombic-I symmetry of the centre. The principal g -values, which are $g_{[110]} = 1.3867$, $g_{[1\bar{1}0]} = 1.4266$ and $g_{[001]} = 2.0789$, respectively, deviate significantly from the pure spin value $g = 2.0023$, indicating substantial contributions from orbital momentum. The g -tensor data were analysed on a model of one electron, with spin $S = 1/2$, in an orbital triplet state, $L = 1$. Spin-orbit coupling and crystal field interactions of cubic, tetragonal or orthorhombic symmetry were included in the model. The theoretical analysis can account in a satisfactory manner for the experimentally observed values. The electronic structure of Pt⁻ is concluded to be the $5d^9 6s 6p$ configuration. This is consistent with predominant bonding of platinum with two silicon neighbours and dihedral distortion. The results are incompatible with alternative models, such as the vacancy model or a $5d$ -version of the Ludwig-Woodbury model. The orbital g -factor is reduced by about 30% by covalency.

1. Introduction

Already in 1962 the electron paramagnetic resonance (EPR) spectrum of platinum as a substitutional impurity in silicon was reported by Woodbury and Ludwig [1]. In the same paper the EPR observation of the corresponding $4d$ transition element, palladium, was also reported. Earlier already, the counterpart in the $3d$ series of transition elements, nickel, was observed by EPR in germanium [2]. Only recently, this impurity was detected by EPR in silicon [3, 4]. The g -tensor components of the spectra in silicon are given in Table I. In this table the g -tensor data for the negatively charged lattice vacancy [5] and the oxygen-vacancy complex [6] are also included. A similarity between these centres has been noted [7]. All spectra indicate orthorhombic-I symmetry, crystallographic point group $2mm(C_{2v})$, of the corresponding centre. All centres are thought to exist in the negatively charged state. On the basis of these observations the vacancy model to describe the electronic structure of these centres was proposed. Inspection of the data given in Table I also reveals that while the principal g -values of the vacancy V⁻ and the oxygen-vacancy complex OV⁻ are close to the free-electron g -value $g = 2.0023$, the values for nickel Ni⁻, palladium Pd⁻ and platinum Pt⁻ do deviate significantly from the free-electron value. This deviation, which is greatest for platinum, may be taken as an indication that the electrons in the d -shell of the transition element are actively involved in determining the electronic character of the centre.

The data given in Table I were obtained by analysing the spectra with the simple Zeeman spin-Hamiltonian $H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$, with electron spin $S = 1/2$. Even with this lowest spin the g -values for platinum were found to be smaller than 2. The amount of magnetic moment $\mu = \mu_B \mathbf{g} \cdot \mathbf{S}$ associated with this centre is therefore quite small. This suggests that an analysis in a model with one electron or hole, the smallest number, and correspondingly $S = 1/2$, should be

appropriate. To account for the deviations of g from 2 orbital momentum must be included, the smallest amount then is $L = 1$. In the next paragraph an analysis on this basis is presented.

2. Mathematical analysis g -tensor

2.1. Approximation cubic

In a provisional crude approximation the centre and its associated g -tensor are treated as isotropic. Spin-orbit interaction $H_{so} = g_L \lambda \mathbf{L} \cdot \mathbf{S}$ will couple the orbital triplet states $L = 1$ and the spin doublet states $S = 1/2$ to a Γ_7 doublet with effective spin $J = 1/2$ and energy $-g_L \lambda$, and a Γ_8 quartet with spin $J = 3/2$ and energy $+g_L \lambda/2$. The g -factors for the coupled orbital and spin momentum are given by a formula of the Landé type:

$$g_J = +g_S[J(J+1) - L(L+1) + S(S+1)]/2J(J+1) + g_L[J(J+1) + L(L+1) - S(S+1)]/2J(J+1). \quad (1)$$

For the present case with $L = 1$ and $S = 1/2$ one obtains for $J = 1/2$: $g_J = +4g_L/3 - g_S/3$, and for $J = 3/2$: $g_J = +2g_L/3 + g_S/3$. In the EPR experiment the sign of either of the principal g -values is not determined. Taking all principal values negative the isotropic average is $g_J = (g_{[110]} + g_{[1\bar{1}0]} + g_{[001]})/3 = -1.6307$. With the intrinsic spin g -value $g_S = 2.0023$ this leads to $g_L = -0.7231$ for the $J = 1/2$ doublet state. For the other ground state, $J = 3/2$, or for other choices of signs of g -values, the solutions appear to be less realistic. The preferred solution as given above has both negative orbital g -factor g_L and spin-orbit coupling constant λ .

2.2. Approximation tetragonal

By inspection of Table I one observes that the Si-Pt(I) spectrum satisfies to very good approximation the criteria for a tetragonal centre. A Hamiltonian to account for a crystal field of such symmetry is

$$H_{tc} = +\Delta_{tc}(2/3 - L_z^2). \quad (2)$$

As before the spin-orbit interaction is given by the Hamiltonian

$$H_{so} = +g_L \lambda \mathbf{L} \cdot \mathbf{S}. \quad (3)$$

Six basis states representing the orbital triplet and spin doublet are:

$$|\Phi_x, +1/2\rangle, |\Phi_y, +1/2\rangle, |\Phi_z, +1/2\rangle, \\ |\Phi_x, -1/2\rangle, |\Phi_y, -1/2\rangle, |\Phi_z, -1/2\rangle.$$

Operation of the Hamiltonian as given by eqs. (2) and (3) on

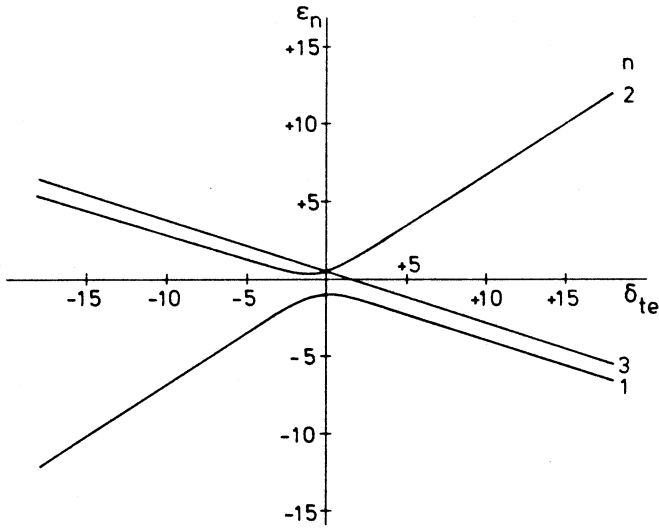


Fig. 1. Energies as a function of the tetragonal crystal field, all quantities in units $g_L \lambda$, for the three doublets, labelled $n = 1, 2$ and 3 .

the six basis states gives the matrix

	$ +\Phi_x, -1/2\rangle$	$ +i\Phi_y, -1/2\rangle$	$ +\Phi_z, +1/2\rangle$
	$ -\Phi_x, +1/2\rangle$	$ +i\Phi_y, +1/2\rangle$	$ +\Phi_z, -1/2\rangle$
$\langle +\Phi_x, -1/2 $	$-\Delta_{te}/3$	$-g_L \lambda/2$	$-g_L \lambda/2$
$\langle -\Phi_x, +1/2 $			
$\langle -i\Phi_y, -1/2 $	$-g_L \lambda/2$	$-\Delta_{te}/3$	$-g_L \lambda/2$
$\langle -i\Phi_y, +1/2 $			
$\langle +\Phi_z, +1/2 $	$-g_L \lambda/2$	$-g_L \lambda/2$	$+2\Delta_{te}/3$
$\langle +\Phi_z, -1/2 $			

The dimension of the matrix is only 3×3 and the levels are doublets as the result of Kramers degeneracy. In the present axial case the introduction of new wave functions for the orbital part facilitates the solution. One thus defines:

$$|+1\rangle \equiv -(+|\Phi_x\rangle + i|\Phi_y\rangle)/\sqrt{2}, \quad (4a)$$

$$|0\rangle \equiv +|\Phi_z\rangle, \quad (4b)$$

$$|-1\rangle \equiv +(+|\Phi_x\rangle - i|\Phi_y\rangle)/\sqrt{2}. \quad (4c)$$

It is convenient to express energies as dimensionless quantities by the definitions $\epsilon_n \equiv E_n/g_L \lambda$ and $\delta_{te} \equiv \Delta_{te}/g_L \lambda$. Solutions for the energies of the three doublets, the corresponding

Table I. Principal g -values of $Si:Pt^-$ and related centres

Centre	Symmetry	$g_{[110]}$	$g_{[1\bar{1}0]}$	$g_{[001]}$
V^-	2 mm	2.0028	2.0151	2.0038
OV^-	2 mm	2.0025	2.0093	2.0031
Ni^-	2 mm	2.0179	2.0532	2.0162
Pd^-	2 mm	1.9715	1.9190	2.0544
Pt^-	2 mm	1.3867	1.4266	2.0789

wave functions and the g -values are then summarized by:

$$n = 1, 2: \epsilon_n = +\delta_{te}/6 - 1/4$$

$$+ (-1)^n (+4\delta_{te}^2 + 4\delta_{te} + 9)^{1/2}/4, \quad (5a)$$

$$|+1/2\rangle = +a_n|+1, -1/2\rangle + b_n|0, +1/2\rangle, \quad (5b)$$

$$|-1/2\rangle = +a_n|-1, +1/2\rangle + b_n|0, -1/2\rangle, \quad (5c)$$

$$a_n = +(1/\sqrt{2})[+1/2 + (+\epsilon_n + \delta_{te}/3 + 1/2)^{1/2}], \quad (5d)$$

$$b_n = +(+\epsilon_n + \delta_{te}/3 + 1/2)/[+1/2 + (+\epsilon_n + \delta_{te}/3 + 1/2)^{1/2}], \quad (5e)$$

$$g_{||} = -2a_n^2 + 2b_n^2 + 2a_n^2 g_L, \quad (5f)$$

$$g_{\perp} = -2b_n^2 - 2\sqrt{2}a_n b_n g_L; \quad (5g)$$

$$n = 3: \epsilon_3 = -\delta_{te}/3 + 1/2, \quad (6a)$$

$$|+1/2\rangle = +|+1, +1/2\rangle, \quad (6b)$$

$$|-1/2\rangle = +|-1, -1/2\rangle, \quad (6c)$$

$$g_{||} = +2 + 2g_L, \quad (6d)$$

$$g_{\perp} = 0. \quad (6e)$$

These solutions are a function of the reduced tetragonal field δ_{te} and the orbital g -value g_L .

A graphical presentation of the energies of all three doublets is given in Fig. 1. One notes that depending on the signs of $g_L \lambda$ and δ_{te} each of the doublets may be the ground state. In Figs. 2 and 3 the parallel and perpendicular g -values of doublets 1 and 2, respectively, are plotted. The corresponding figure for doublet $n = 3$ is omitted as eq. (6e) predicts $g_{\perp} = 0$ for this case, which obviously is contrary to the experimental observation for the Si-Pt(I) spectrum. For a con-

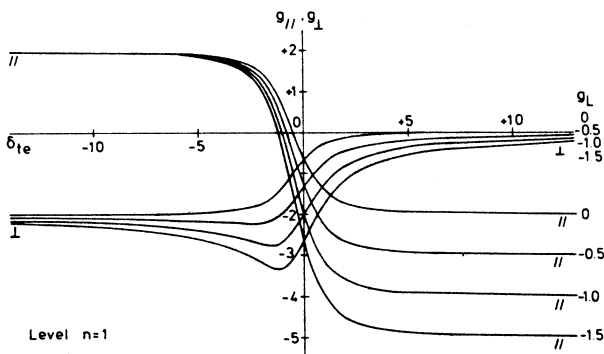


Fig. 2. Parallel ($\parallel$) and perpendicular ($\perp$) g -values as a function of the tetragonal field δ_{te} for some values of the orbital g -factor g_L for doublet $n = 1$.

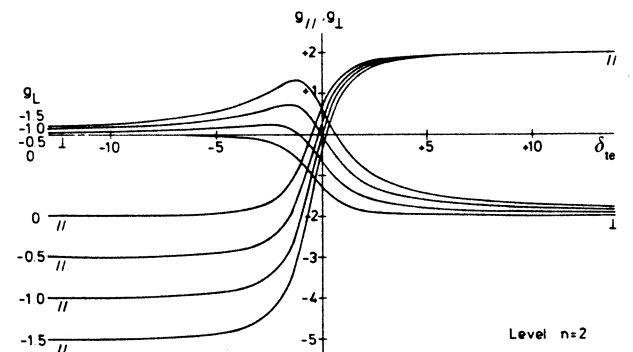


Fig. 3. Parallel ($\parallel$) and perpendicular ($\perp$) g -values as a function of the tetragonal field δ_{te} for some values of the orbital g -factor g_L for doublet $n = 2$.

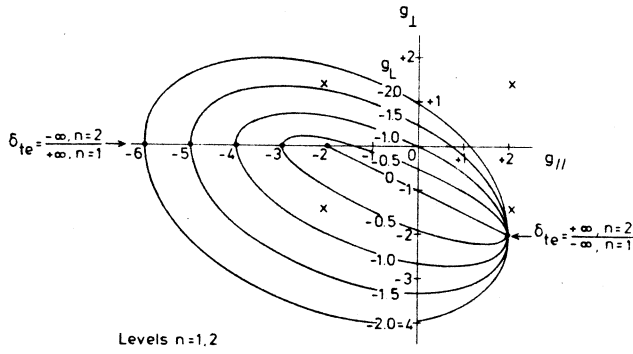


Fig. 4. Relation between the parallel and perpendicular components of the g -tensor, $g_{||}$ and $g_{\perp}$, for some values of the orbital g -factor g_L , for the doublet levels $n = 1$ and 2. Experimental data for the spectrum Si-Pt(I) are also included in the diagram by the symbols $\times$.

venient comparison with the experimental g -values a relation between $g_{||}$ and $g_{\perp}$ can be derived by elimination of δ_{te} from eqs. (5) and (6). Figure 4 shows the result for the doublets 1 and 2 for some values of the orbital g -factor g_L . Experimental values for the spectrum Si-Pt(I) are also included in this figure. The principal values of the orthorhombic g -tensor are converted to the tetragonal approximation by putting $g_{||} = g_{[001]} = \pm 2.0789$ and $g_{\perp} = (g_{[110]} + g_{[1\bar{1}0]})/2 = \pm 1.4067$. Best agreement with physically meaningful and consistent values of the parameters are obtained for doublet $n = 1$ and negative values of $g_{||}$ and $g_{\perp}$. The relevant region in the $(g_{||}, g_{\perp})$ -plane is shown on enlarged scale in Fig. 5. The solution gives $\delta_{te} = +0.302$ and $g_L = -0.732$ for the Si-Pt(I) centre. It may be emphasized that in the analysis as presented two unknown parameters in the theory, δ_{te} and g_L , are calculated from two parameters, $g_{||}$ and $g_{\perp}$, which were determined experimentally. The solution following this procedure is exact.

2.3. Approximation orthorhombic

As the actual symmetry of the Si-Pt(I) centre is orthorhombic it is desirable to extend the analysis to this more general case. To the Hamiltonian $H_{te} + H_{so}$ a term is added representing the orthorhombic crystal field

$$H_{rh} = +\Delta_{rh}(L_x^2 - L_y^2). \quad (7)$$

The matrix to be diagonalised becomes

	$ +\Phi_x, -1/2\rangle$	$ +\Phi_y, -1/2\rangle$	$ +\Phi_z, +1/2\rangle$
$ +\Phi_x, -1/2\rangle$	$-\Delta_{te}/3 - \Delta_{rh}$	$-g_L\lambda/2$	$-g_L\lambda/2$
$ +\Phi_y, -1/2\rangle$	$-g_L\lambda/2$	$-\Delta_{te}/3 + \Delta_{rh}$	$-g_L\lambda/2$
$ +\Phi_z, +1/2\rangle$	$-g_L\lambda/2$	$-g_L\lambda/2$	$+2\Delta_{te}/3$

Solutions are summarized below. Energies in reduced units are defined as $\delta_{te} \equiv \Delta_{te}/g_L\lambda$, $\delta_{rh} \equiv \Delta_{rh}/g_L\lambda$ and $\epsilon_n \equiv E_n/g_L\lambda$. The energies of the three doublets are given by

$$\epsilon_n = + (1/3)(+4\delta_{te}^2 + 12\delta_{rh}^2 + 9)^{1/2} \cos[(\phi + 2n\pi)/3], \quad (8a)$$

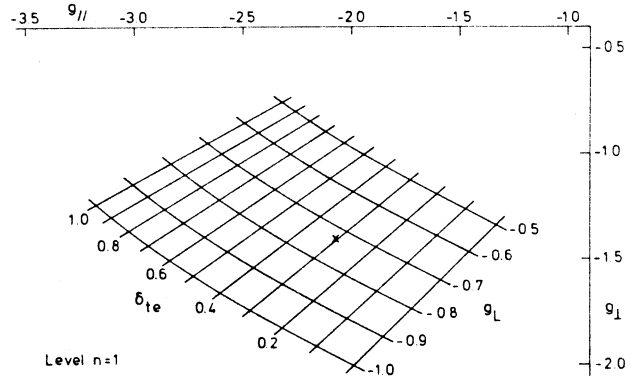


Fig. 5. As in Fig. 4. Close-up view, with also the axial field δ_{te} indicated, showing the fit of the principal values of spectrum Si-Pt(I) for $\delta_{te} = +0.302$ and $g_L = -0.732$.

with

$$\cos \phi = + (8\delta_{te}^3 - 72\delta_{te}\delta_{rh}^2 - 27) / (+4\delta_{te}^2 + 12\delta_{rh}^2 + 9)^{3/2}. \quad (8b)$$

Wave functions are expanded as

$$|+1/2\rangle = +a_n|-\Phi_x, +1/2\rangle + b_n|+i\Phi_y, +1/2\rangle + c_n|+\Phi_z, -1/2\rangle, \quad (9a)$$

$$|-1/2\rangle = +a_n|+\Phi_x, -1/2\rangle + b_n|+i\Phi_y, -1/2\rangle + c_n|+\Phi_z, +1/2\rangle. \quad (9b)$$

The coefficients in the expansion are

$$a_n = +N_n(+\delta_{te}/3 - \delta_{rh} - 1/2 + \epsilon_n), \quad (10a)$$

$$b_n = +N_n(+\delta_{te}/3 + \delta_{rh} - 1/2 + \epsilon_n), \quad (10b)$$

$$c_n = +N_n(-2\delta_{te}^2/9 + 2\delta_{rh}^2 - 4\delta_{te}\epsilon_n/3 - 2\epsilon_n^2 + 1/2). \quad (10c)$$

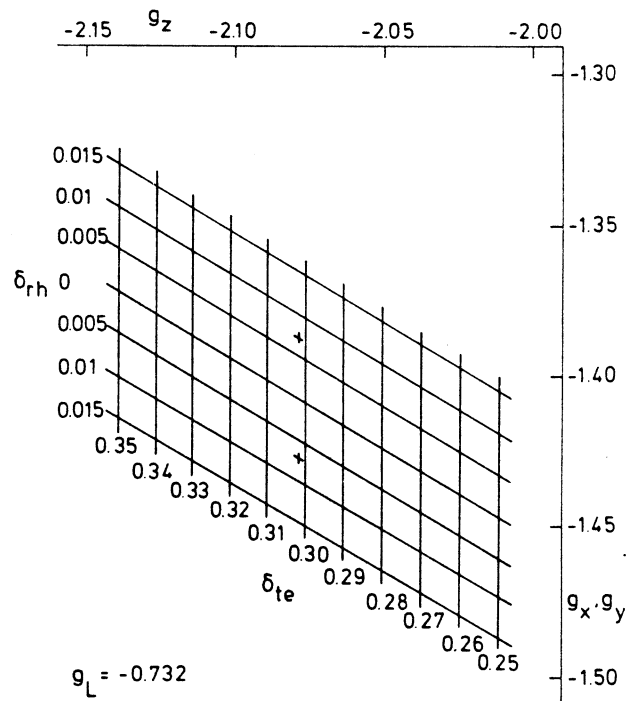


Fig. 6. Principal values g_x , g_y and g_z for several values of the crystal fields δ_{te} and δ_{rh} , orbital g -factor $g_L = -0.732$. The fit for the Si-Pt(I) spectrum for $\delta_{te} = +0.302$ and $\delta_{rh} = +0.007$ is shown.

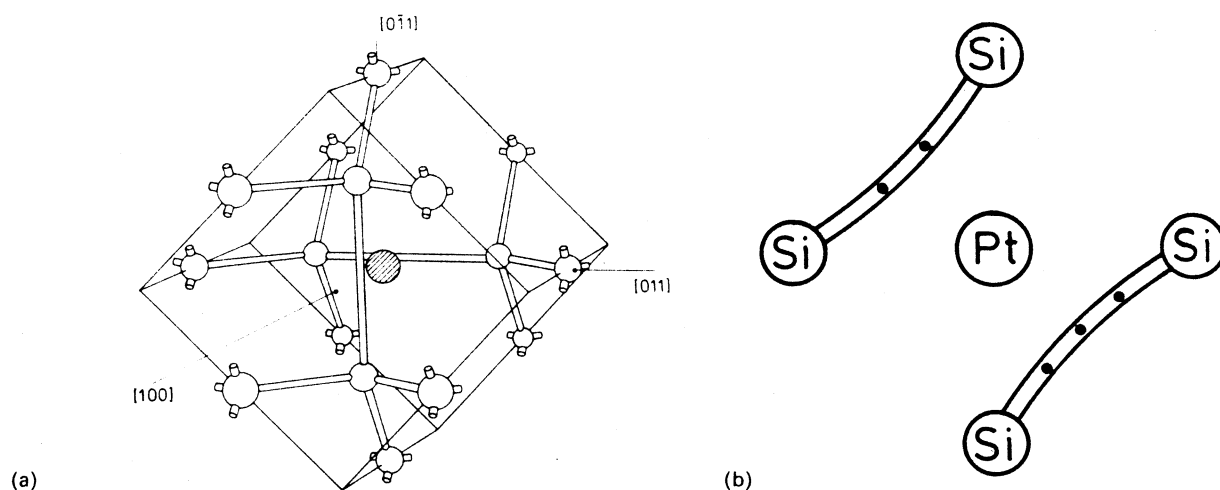


Fig. 7. Electronic structure for negative substitutional platinum in silicon in the vacancy model. (a) Stereographic and (b) more schematic 2-dimensional representation of the structure.

with normalisation constant N_n . The g -values are expressed in the wave function coefficients by

$$g_x = +2a_n^2 - 2b_n^2 - 2c_n^2 + 4b_n c_n g_L, \quad (11a)$$

$$g_y = -2a_n^2 + 2b_n^2 - 2c_n^2 + 4a_n c_n g_L, \quad (11b)$$

$$g_z = -2a_n^2 - 2b_n^2 + 2c_n^2 + 4a_n b_n g_L. \quad (11c)$$

As in the previous case, the number of parameters in the theory to be determined is equal to the number of g -values from the experiment. In the orthorhombic case the three principal g -values $g_{[110]}$, $g_{[1\bar{1}0]}$ and $g_{[001]}$ lead to unique values for δ_{ic} , δ_{rh} and g_L . When a solution exists, it will be exact. For the Si-Pt(I) spectrum the result is $\delta_{ic} = +0.302$, $\delta_{rh} = +0.007$ and $g_L = -0.732$. The graphical illustration of the solution is given in Fig. 6.

3. Physical interpretation

3.1. Vacancy model

The Si-Pt(I) spectrum is interpreted as arising from a single platinum atom, on a substitutional site in the silicon crystal, in a negatively charged state. Several experimental observations on the spectrum, such as its formation, stability,

reorientation effects and ^{195}Pt hyperfine structure, support the identification [1, 8]. The equivalent centres and EPR spectra for nickel and palladium are also known [1, 3, 4]. Regarding their detailed electronic structure striking parallels between these transition element impurities and the negative lattice vacancy have been pointed out [7]. In the vacancy model, which was proposed on the basis of this evidence, the transition element has a full d -shell, accommodating 10 electrons. The remaining electron will occupy an anti-bonding orbital between two silicon nearest-neighbour atoms. The model for the electronic configuration of substitutional Pt^- is $\text{Pt}(5d^{10}) + V^-$. Its structure is illustrated in Fig. 7. Having a closed d -shell the transition metal impurity has little effect on the electronic properties. Rather the electronic properties of the centre will be very much like the negative vacancy. The model provides a natural explanation for the spin $S = 1/2$ of all these centres, the dihedral distortion which they have in common, and the motional effects between orientations of distortion. All centres have, like the vacancy, deep levels which are effective recombination centres. In the model the unpaired electron occupies an orbital singlet anti-bonding state. This state will be intermixed with other states derived from the vacancy t_2 level by the spin-orbit interaction. On

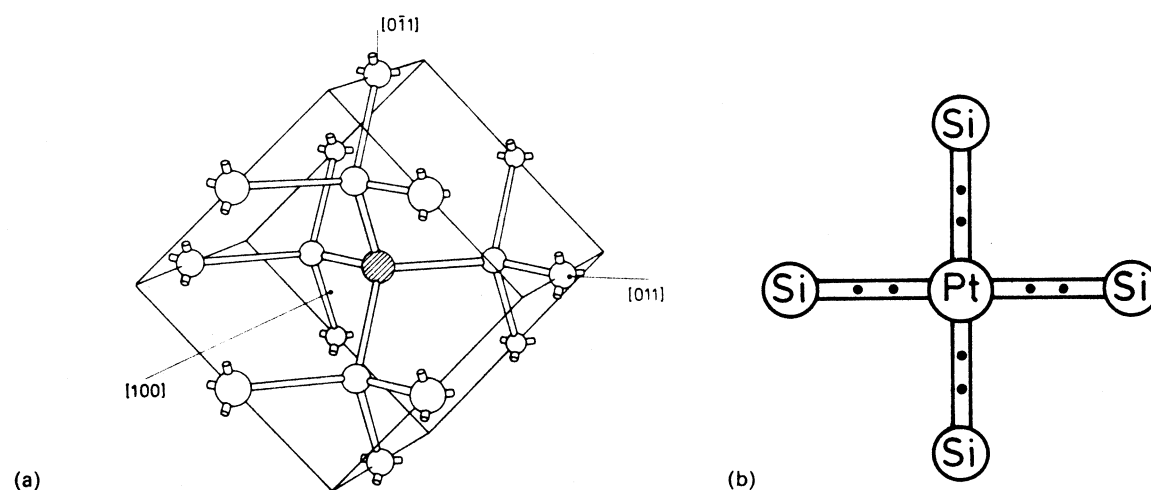


Fig. 8. Electronic structure for negative substitutional platinum in silicon in the Ludwig-Woodbury model for $5d$ electrons. (a) Stereographic and (b) more schematic 2-dimensional representation of the structure.

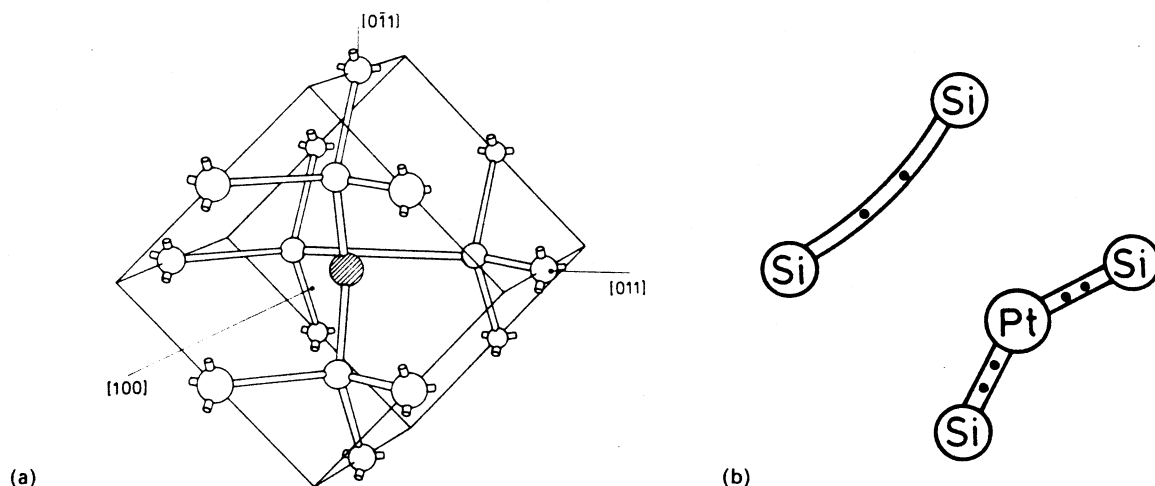


Fig. 9. Electronic structure for negative substitutional platinum in silicon in the two-neighbour-bonding model. (a) Stereographic and (b) more schematic 2-dimensional representation of the structure.

this basis Lowther has been able to account for the observed g -values [9]. It is necessary to assume a spin-orbit coupling strength comparable to the orthorhombic crystal field splitting. Actually, for the vacancy the g -values are close to $g = 2$, indicating effective quenching of orbital momentum by the crystal field forces. The state is more appropriately described by $L = 0$. The oxygen-vacancy complex has a very similar structure [10]. For platinum, however, the deviations of the g -values from 2 are quite substantial. The previous analysis has shown that these can be understood starting from $L = 1$ and taking quenching by crystal fields properly into account. It is concluded that the vacancy model does not provide the natural basis for the electronic properties of platinum as revealed by its g -tensor.

3.2. Ludwig-Woodbury model

A successful model to account for the electronic properties of 3d transition metal impurities in silicon was proposed by Ludwig and Woodbury [11]. In the model the substitutional impurities are fully tetrahedrally bonded to four nearest neighbour silicon atoms, as illustrated in Fig. 8. For negative substitutional platinum this leaves 7 electrons in the 5d shell. The occupation of one-electron orbitals, both for high or low spin coupling, is given in Fig. 10(a). This scheme predicts an undistorted tetrahedral centre with orbital momentum $L = 0$

and spin $S = 3/2$. Such a prediction is at variance with the conclusions derived from the experiment.

3.3. Two-neighbour-bonding model

Intermediate between the previous cases of no or full tetrahedral bonding, one may consider bonding to two silicon neighbour atoms. The model is illustrated by Fig. 9. For the 5d shell 9 electrons are left which occupy the one-electron orbitals as given in Fig. 10(b). This naturally leads to $L = 1$ and $S = 1/2$, in agreement with the presupposition in the analysis. The Jahn-Teller instability is lifted by the dihedral distortion.

In this model the paramagnetism is associated with a hole in the 5d shell. The orbital g -factor for this case gives a theoretical $g_L = -1$, comparing favourably with the value $g_L = -0.732$ obtained from the analysis. The difference can be related to some covalent delocalisation of the hole.

For a free platinum ion in configuration $5d^9$ the spin-orbit constant $\lambda = -418$ meV is estimated from the optical spectrum [12]. With this value one calculates $\Delta_{ic} = +0.302g_L\lambda = +92$ meV and $\Delta_{th} = +0.007g_L\lambda = 2.2$ meV.

4. Conclusion

The paramagnetism of the negative substitutional platinum impurity in silicon is related to one hole in the shell of 5d electrons. An analysis taking into account crystal fields and spin-orbit interaction is given of the g -values observed in electron paramagnetic resonance. The orbital g -factor associated with the hole is slightly reduced by covalency. Two electrons are used to bind the platinum to silicon neighbour atoms, consistent with the orthorhombic symmetry of the centre.

t_2 states		
e states		
Configuration	$5d^7$ ($6s6p^3$)	$5d^9$ ($6s6p$)
Orbital momentum	$L = 0$	$L = 1$
Spin	$S = 3/2$	$S = 1/2$
	(a)	(b)

Fig. 10. Occupation of the one-electron levels derived from the 5d orbitals in tetrahedral symmetry by (a) 7 electrons in the fully tetrahedrally bonded model, and (b) 9 electrons for bonding with 2 silicon neighbour atoms.

References

1. Woodbury, H. H. and Ludwig, G. W., Phys. Rev. **126**, 466 (1962).
2. Ludwig, G. W. and Woodbury, H. H., Phys. Rev. **113**, 1014 (1959).
3. Vlasenko, L. S., Lebedev, A. A., Tapygov, E. S. and Khramtsov, V. A., Sov. Techn. Phys. Lett. **13**, 1322 (1987).
4. Vlasenko, L. S., Son, N. T., van Oosten, A. B., Ammerlaan, C. A. J., Lebedev, A. A., Tapygov, E. S. and Khramtsov, V. A., Solid State Commun. (to be published).
5. Watkins, G. D., in Radiation Damage in Semiconductors, (Edited by P. Baruch), p. 97, Dunod, Paris (1965).

6. Watkins, G. D. and Corbett, J. W., *Phys. Rev.* **121**, 1001 (1961).
7. Watkins, G. D., *Physica* **117B&118B**, 9 (1983).
8. Milligan, R. F., Anderson, F. G. and Watkins, G. D., *Phys. Rev.* **B29**, 2819 (1984).
9. Lowther, J. E., *J. Phys. C: Solid State Phys.* **13**, 3681 (1980).
10. Van Kemp, R., Sieverts, E. G. and Ammerlaan, C. A. J., *Mat. Sci. Forum* **10-12**, 875 (1986).
11. Ludwig, G. W. and Woodbury, H. H., *Phys. Rev. Lett.* **5**, 98 (1960).
12. Moore, C. E., in *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467, Volume III (1958).