

Vacancy-model-based electronic structure of the Pt⁻ impurity in silicon

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We present here a detailed model for the electronic structure of the Pt⁻ impurity in silicon that is consistent with both experimental results and the results of self-consistent empirical tight-binding Green's-function calculations for the on-center and the distorted Pt impurities. This model is based on the electronic structure for this impurity as prescribed by Watkins' vacancy model.

I. INTRODUCTION

A detailed model for the electronic structure of isolated substitutional transition-metal (TM) impurities in silicon that is consistent with both experimental and computational results has been until now elusive. Watkins has proposed a vacancy model,¹ which predicts in general terms the electronic structures of substitutional TM impurities at the heavy end of each row in the TM series. This model is supported by the results of several computational works.²⁻⁶ However, a detailed electronic structure based on the vacancy model has not been presented. In contrast to this, based on the results of their electron-paramagnetic resonance and electron-nuclear-double resonance experiments investigating the Pt⁻, Pd⁻, and Ni⁻ impurities in silicon, Ammerlaan and Van Oosten recently concluded that the vacancy model fails to predict the correct electronic structure of these defects, and have proposed a dihedral model in place of the vacancy model.⁷ Here, we present a detailed study of the electronic structure of the Pt⁻ impurity in silicon which shows that the vacancy model can account for the experimental situation. We first use a simplified analytical description whose parameters are chosen in order to achieve a fit to the experimental g values and central-hyperfine constants.^{7,8} We then present a full self-consistent Green's-function calculation for both the on-center and the distorted Pt⁰ impurities in silicon, which confirms the validity of the simple picture and shows that its parameters are quite reasonable.

As noted by Hemstreet,² the creation of a substitutional impurity is a two-step process. The first step is the creation of a host-atom vacancy; the second is to place the impurity atom in this vacancy and to turn on the interaction between the impurities valence orbitals and the $|a_1\rangle$, $|t_2\rangle$ vacancy orbitals that are linear combinations of the four silicon dangling bonds. For the TM impurities, various computations have shown the following results:²⁻⁶ the $|a_1\rangle$ vacancy orbital is largely unaffected; the impurities d orbitals of e symmetry, which remain very localized on the impurity atom, are found in either the band gap or the valence band. In contrast to this, the impurities d orbitals of t_2 symmetry mix with the vacancy orbitals of the same symmetry giving rise to bonding and antibonding states. The bonding t_2 manifold (t_{2B}) is found fully occupied in the valence band, while the antibonding manifold (t_{2AB}) is

found either in the band gap or in the conduction band.

The vacancy model can be used to describe the electronic structure of TM impurities, such as Pt, at the heavy end of each row of the TM series. In these cases, the d orbitals lie deep within the valence band, and the interaction between the impurity t_2 orbitals and the vacancy t_2 orbitals is rather weak, though not insignificant as we demonstrate in this work. Thus, the orbitals of the t_{2B} manifold are very localized on the impurity atom, while the orbitals of the t_{2AB} manifold are essentially the t_2 vacancy orbitals, and possess only a small degree of localization on the impurity atom. The Pt⁻ impurity has a total of three electrons in the t_{2AB} manifold. Hence, we would expect that the Pt⁻ impurity should have characteristics similar to those of the V^- defect and, like the V^- , this impurity has C_{2v} point symmetry and an effective spin $S = \frac{1}{2}$.^{7,8} These results show the early success of the vacancy model.¹

II. ELECTRONIC STRUCTURE ANALYTIC MODEL

We now detail a simple model that can be employed for the electronic structure of the Pt⁻ impurity. As a starting point for this model, we use the results of the vacancy model. The C_{2v} point symmetry of this impurity, like that of the V^- , is a result of two static Jahn-Teller distortions: a tetragonal distortion (defining a particular cubic axis as the z axis) and a trigonal distortion. The final result of these distortions is that, in terms of the cubic axis directions, the principal axes are $x \sim [110]$, $y \sim [-110]$, $z \sim [001]$. Taking into account the symmetry of the defect, it is convenient to write the orbitals of the t_{2AB} and e manifolds using the principal axis direction x, y, z . From the three states spanning the t_{2AB} manifold, we can build three states which transform like a_1 , b_1 , and b_2 in C_{2v} symmetry. Because of the mixed distortion, these states are no longer degenerate (Fig. 1). In accordance with the vacancy model, a small amount (γ^2) of each of these orbitals is localized on the impurity atom. The symmetry of the d orbital associated with each of these three orbitals is given by $|zx\rangle(b_1)$, $|yz\rangle(b_2)$, and $|x^2 - y^2\rangle(a_1)$. In the same manner, the e states transform like $a_2(|xy\rangle)$ and $a_1(|3z^2 - r^2\rangle)$ in C_{2v} symmetry. Therefore, we must include a small but important mixing of the $|3z^2 - r^2\rangle d$ orbital in the $|a_1\rangle$ state derived from the t_{2AB} manifold. In

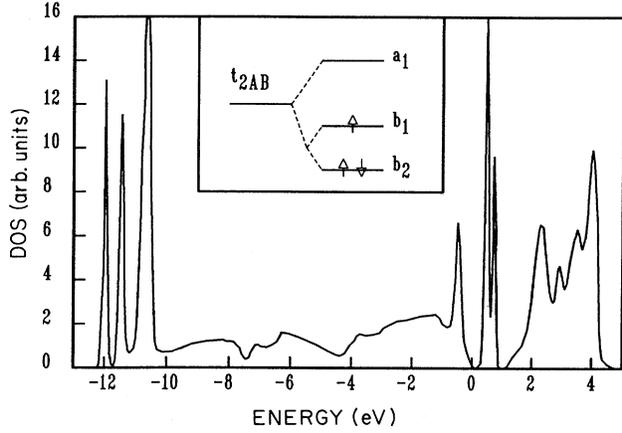


FIG. 1. The total DOS plot for the distorted configuration of the Pt^0 impurity. The zero of energy corresponds to the top of the valence band. See the text for a description of the origins of the various peaks. Inset: the two Jahn-Teller distortions completely lift the orbital degeneracy of the t_{2AB} manifold. The ordering of the levels is deduced from the fit of the experimental g and A values. These orbitals are occupied by three electrons, as indicated, resulting in an effective spin $S = \frac{1}{2}$.

summary, the components on the d orbitals of the three gap states are

$$\begin{aligned} |b_1\rangle &\sim |zx\rangle, \\ |b_2\rangle &\sim |yz\rangle, \\ |a_1\rangle &\sim \cos(\beta)|x^2 - y^2\rangle + \sin(\beta)|3z^2 - r^2\rangle, \end{aligned} \quad (1)$$

where β accounts for the mixing. Then we can calculate the matrix of the total Hamiltonian—crystal-field plus spin-orbit—in the basis $(a_1, \bar{a}_1, b_1, \bar{b}_1, b_2, \bar{b}_2)$. We make the approximation that the spin-orbit interaction in the t_{2AB} manifold comes entirely from those parts of the orbitals localized on the impurity atom. Using the same formalism as Lowther,⁹ it is easy to show that the Hamiltonian can be simplified in two identical blocks by a convenient basis change. The block in the basis $(\bar{a}_1, b_1, i\bar{b}_2)$ or $(-a_1, \bar{b}_1, -i\bar{b}_2)$ is

$$\begin{pmatrix} E_{a_1} & -\frac{\gamma^2 \lambda u}{2} & -\frac{\gamma^2 \lambda v}{2} \\ -\frac{\gamma^2 \lambda u}{2} & E_{b_1} & \frac{\gamma^2 \lambda}{2} \\ -\frac{\gamma^2 \lambda v}{2} & \frac{\gamma^2 \lambda}{2} & E_{b_2} \end{pmatrix}, \quad (2)$$

where $u = \cos(\beta) - \sqrt{3}\sin(\beta)$ and $v = \cos(\beta) + \sqrt{3}\sin(\beta)$. Therefore the resulting eigenfunctions for the spin unpaired electron can be written as

$$|\uparrow\rangle = \cos(\alpha)\cos(\theta)|b_1\rangle - i\cos(\alpha)\sin(\theta)|b_2\rangle + \sin(\alpha)|\bar{a}_1\rangle, \quad (3)$$

$$|\downarrow\rangle = \cos(\alpha)\cos(\theta)|\bar{b}_1\rangle + i\cos(\alpha)\sin(\theta)|\bar{b}_2\rangle - \sin(\alpha)|a_1\rangle,$$

where $\cos(\alpha)$ and $\cos(\theta)$ are defined to be positive. By following the nonperturbative formalism of Lowther,⁹ we obtain expressions for the g values and the central-

hyperfine constants. This involves determining the matrix elements of the Zeeman and the central-hyperfine interactions taken between the many-electron states making up the effective spin $S = \frac{1}{2}$ manifold. Doing this for the g values, we can easily show that we need only to calculate the matrix elements of the one-electron Zeeman interaction taken between the states $|\uparrow\rangle$ and $|\downarrow\rangle$. We find that the principal g values are given by ($g_0 = 2.0023$)

$$\begin{aligned} g_x &= g_0[-\sin^2(\alpha) + \cos^2(\alpha)\cos(2\theta)] \\ &\quad - 2v\gamma^2\sin(2\alpha)\sin(\theta), \\ g_y &= g_0[\sin^2(\alpha) + \cos^2(\alpha)\cos(2\theta)] \\ &\quad - 2u\gamma^2\sin(2\alpha)\cos(\theta), \\ g_z &= g_0\cos(2\alpha) - 2\gamma^2\cos^2(\alpha)\sin(2\theta). \end{aligned} \quad (4)$$

We are assuming in Eq. (4) that the orbital momentum, as well as the spin-orbit interaction, comes entirely from those parts of the t_{2AB} orbitals localized on the impurity atom. Contributions from the ligands to the orbital momentum are smaller because they only involve terms between orbitals of distinct atoms. The g values for the Pt^- impurity are very much different from the g values of the V^- defect, suggesting that the Pt impurity itself is actively involved. Equation (4) shows that the large departures of g_x and g_y from g_0 are *not* a result of the orbital term to the Zeeman interaction, but rather, are a result of a strong mixing by the spin-orbit interaction of the $|b_1\rangle$ and $|b_2\rangle$ orbitals. The orbital term of the Zeeman interaction is responsible for the difference between g_x and g_y .

With Eq. (4), the four parameters γ^2 , α , θ , and β cannot be determined unequivocally from the experimental g values. Therefore one must also consider the central-hyperfine terms. The latter have three components: the contact term, the orbital term, and the dipole-dipole term. The contact term ($A_c \mathbf{I} \cdot \mathbf{S}$), which results from core polarization, is treated as an additional parameter. The orbital term can be treated in the same fashion as the orbital term of the Zeeman interaction. We assume that the factor $\langle r^{-3} \rangle$ appearing in this term is simply the atomic value reduced by the degree of localization on the impurity atom, γ^2 .¹⁰ The matrix elements of the dipole-dipole term are calculated within the same formalism as before for the matrix elements of the Zeeman interaction. We consider in this term only the contribution coming from the unpaired electron. The calculation of the orbital and dipole-dipole terms gives complex analytical expressions depending on γ^2 , β , α , and θ . Details will be given in a future paper.¹¹ Because of polarization effects, there are contributions to the orbital and the dipole-dipole terms from the spin-paired electrons. Because of the differences in the factor $\langle r^{-3} \rangle$ for the two spin states of the spin-paired electrons, the contributions coming from the two spin states no longer cancel. Thus, there is an additional contribution to the central-hyperfine interaction. The details show that this additional contribution is restricted to the z direction. We denote this contribution A_{pol} , which we treat as a parameter.

The six parameters γ^2 , α , θ , β , A_c , and A_{pol} of our analytical model can be determined unequivocally from

TABLE I. Values for the various parameters that we used to fit our model of the electronic structure of the Pt^- impurity in silicon to the experimental results of Refs. 7 and 8.

$\gamma^2=0.14,$	$\alpha=0.17$
$\theta=-0.39,$	$\beta=0.44$
$A_c=-165.97 \times 10^{-4} \text{ cm}^{-1}$	
$A_{\text{pol}}=-82.48 \times 10^{-4} \text{ cm}^{-1}$	

the measured g values and central hyperfine constants. They are given in Table I and are compared to the results of the Green's-function calculation in Sec. III. From γ^2 , we find that only 14% of each of the t_{2AB} orbitals is localized on the Pt impurity itself. Using the value for the one-electron spin-orbit parameter for Pt with a d^9 configuration ($\lambda=0.5$ eV), we calculate from Eqs. (2) and (3) the energy splitting between the $|a_1\rangle$ orbital and the $|b_1\rangle$ and $|b_2\rangle$ orbitals— $(E_{a_1}-E_{b_1})$ and $(E_{a_1}-E_{b_2})$ —that results from the Jahn-Teller distortion to be 0.17 and 0.22 eV, respectively. The final ordering of these three levels is shown in Fig. 1 and is found to be opposite to what is found for V^- , as given in Ref. 1. In fact, the vacancy model can only predict the possibility of tetragonal and trigonal distortions, but it cannot predict from symmetry alone the senses of the splittings. We note that the unpaired electron is always found in the $|b_1\rangle$ state. Therefore, the dominant silicon hyperfine interaction is in the xz plane, in agreement with the experimental results of Woodbury and Ludwig.⁸ Finally, from the value of β , we find that the character of that part of the $|a_1\rangle$ orbital localized on the Pt impurity itself is 18% $|3z^2-r^2\rangle$ -like.

III. COMPUTATIONAL RESULTS

We now consider the results of our self-consistent empirical tight-binding Green's-function calculations for the on-center and the distorted Pt^0 impurity. These calculations are done in the same spirit as those of Delerue *et al.* for the on-center $3d$ TM impurities.⁶ The energy of the impurity d orbitals (E_d) is linearly dependent on the electronic population of the impurity atom. We have added a potential to each of the four silicon neighbors that is linearly dependent ($U_n=5$ eV/electron) on the electronic population of the particular neighbor. The interatomic matrix elements for the on-center Pt impurity are deduced from Harrison's rules.¹² Those for the distorted impurity are modified in an exponential fashion.¹³ Finally, we impose the condition that the collection of the impurity atom and the four neighbors must be electrically neutral.

For the Pt^0 impurity, there are only two electrons in the t_{2AB} manifold. One of these electrons was placed into the $|b_1\rangle$ orbital, the second into the $|b_2\rangle$ orbital. For the distorted configuration, the impurity atom was displaced 0.6 Å (an arbitrary choice) along the $[001]$ direction. For simplicity, the silicon neighbors were fixed at their usual positions.

The calculated total density of states (DOS) for the distorted configuration is plotted in Fig. 1. The peak in the DOS just below the top of the valence band comes from the $|a_1\rangle$ orbital of the vacancy. The three peaks around

–12 and –10 eV result from the e and t_{2B} manifolds, and are highly localized on the Pt impurity itself. Within the band gap, there are two peaks coming from the t_{2AB} manifold. The large peak, at lower energy, is composed of the $|b_1\rangle$ and $|b_2\rangle$ orbitals; the second peak arises from the $|a_1\rangle$ orbital.

In the on-center configuration, the localization on the Pt^- impurity itself of the orbitals from the t_{2AB} manifold is found to be 13%, in very close agreement with the value of γ^2 in the model of Sec. II. The ordering of the levels, Fig. 1, and the size of the splittings are supported by the results of this calculation. Finally, our computational results showed that for this distortion, the character of that part of the $|a_1\rangle$ orbital localized on the Pt impurity itself is 22% $|3z^2-r^2\rangle$ -like, in close agreement with the value used in the fit of Sec. II. While we do not want to suggest that our computational results are quantitatively very accurate, we do believe that they serve as a general guide for the size of the various parameters that we have incorporated into our model.

IV. DISCUSSION AND CONCLUSION

Our results show that the vacancy model does indeed prescribe the correct electronic structure for the Pt^- impurity in silicon. This conclusion is in contrast to that reached by Ammerlaan and Van Oosten.⁷ The dihedral model proposed by these authors is essentially the Ludwig and Woodbury model for the substitutional TM impurities in silicon,¹⁴ but modified in such a way that the bonding is only to two of the silicon neighbors instead of four. This leaves the Pt impurity itself in a d^9 configuration. This open shell configuration is the source of the relatively large amount of orbital momentum that is required in their model to explain the large shifts of g_x and g_y from g_0 that are found for the Pt^- impurity. We have demonstrated here that the Pt^- g values can indeed be explained by a model that requires only a relatively small amount of orbital momentum. Even though there is only a small amount of the t_{2AB} orbitals localized on the Pt impurity itself, the spin-orbit interaction for Pt is strong enough to account for the large departures in g_x and g_y from g_0 . If the vacancy model can account for the experimental g and A values, it does not explain the important difference between the ligand hyperfine structure of Pt^- (Ref. 8) and V^- .¹⁵ Nevertheless, the charge density on the ligand orbitals, in particular the s density, is probably very sensitive to the Si atom displacements and, if the distortions in the case of V^- and Pt^- have a similar symmetry, they have not the same nature since a central atom (Pt) is involved in the latter case. But to check this point would require much heavier calculations than those we have done here.

In conclusion, we have presented a detailed model for the electronic structure of the Pt^- impurity in silicon that confirms Watkin's vacancy model. Our model is both in agreement with experimental results and supported by our computational results. These results lead us to believe that this model can be extended to the cases of the Ni^- and Pd^- impurities, which are respectively the $3d$ and $4d$ cases of the Pt^- impurity.

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