

THE ELECTRONIC STRUCTURE OF PLATINUM, PALLADIUM AND NICKEL IN SILICON

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ABSTRACT

Magnetic resonance studies on $\text{Si:}^{105}\text{Pd}^-$ and $\text{Si:}^{61}\text{Ni}^-$ are reported. The observations provide evidence for the transition metal to be a substitutional d^9 -ion, bound to two Si neighbors. With this model recently the g -values of Si:Pt^- were explained. We here propose this model for Si:Ni^- , Ge:Ni^- , Si:Pd^- and Si:Pt^- . Also, we report the identification of Pt(II) as PtFe^- and the observation of its analogue PdFe^- .

INTRODUCTION

Ludwig and Woodbury reported an electron paramagnetic resonance (EPR) study on Ge:Ni^- [1], and also studied Si:Pt^- and Si:Pd^- [2] by EPR. From the dependence of the EPR intensity on the concentration of compensating donors it was concluded that Ge:Ni is a double acceptor, while Si:Pt and Si:Pd are single acceptors. Recently, the analogous Si:Ni^- was discovered [3]. In order to explain the orthorhombic (2mm) symmetry, common to these centers, the vacancy model was proposed [4], in which these centers are thought to be closed shell atoms, situated in a negatively charged lattice vacancy. However, the vacancy model cannot account for the very anisotropic g -tensor of Si:Pt^- , which is nearly $\langle 100 \rangle$ -axial with $g_{\parallel}=2.0789$ and $g_{\perp}=1.4$. Ammerlaan and van Oosten [5] recently proposed the dihedral model, explaining the Si:Pt^- g -values.

In this contribution we first briefly review the dihedral model. Then we present new results on $\text{Si:}^{61}\text{Ni}^-$ and $\text{Si:}^{105}\text{Pd}^-$ that provide evidence for open d -shell paramagnetism in these centers as well. Consequently, we propose that Si:Ni^- , Si:Pd^- and Ge:Ni^- have the dihedral structure in common with Si:Pt^- .

Also, we report the identification of the trigonal Pt(II) center as a PtFe pair. The palladium analogue of this center, PdFe^- , is reported here for the first time.

THE DIHEDRAL MODEL FOR Si:Pt⁻

The dihedral model is based on the idea that the low value of g_L of Si:Pt⁻ indicates the presence of orbital momentum in the center. It assumes the simple case of an electron spin $S=1/2$ interacting with an orbital momentum $L=1$. The orbital momentum is coupled to an orthorhombic crystal field. The hamiltonian is

$$H = \Delta_{te} \left(\frac{2}{3} - L_z^2 \right) + \Delta_{rh} (L_x^2 - L_y^2) + \lambda g_L \vec{L} \cdot \vec{S} \quad (1)$$

This hamiltonian is diagonalized and expressions for $\vec{g}$ are derived in terms of the three parameters Δ_{te} , Δ_{rh} and g_L . The spin-orbit parameter is obtained from atomic data. The experimental g -values are obtained for $g_L = -0.732$, $\Delta_{te} = +92$ meV and $\Delta_{rh} = 2.2$ meV, with $\lambda = -418$ meV. This compares favorably with the case of a hole in a 5d-T₂ state, for which $g_S = +2.0023$ and $g_L = -1$. An electronic structure consistent with this picture is substitutional Pt⁻ in the 3d⁹ configuration, bound to only two out of four Si ligands, with the remaining two Si ligands forming a reconstructed bond.

It is natural to extend the dihedral model to Ge:Ni⁻, Si:Ni⁻ and Si:Pd⁻. However, the g -values of Ge:Ni⁻, Si:Ni⁻ and Si:Pd⁻ are much less anisotropic and do not provide sufficient evidence for the presence of orbital moment in the ground state. It will be seen below that such evidence comes from the nuclear Zeeman interaction.

EPR AND ENDOR OF Si:Pd⁻

Spin resonance of the Si:Pd⁻ center was first observed by Woodbury and Ludwig [2]. Perturbation theory was inadequate for the description of the ¹⁰⁵Pd ($I=5/2$, $q=0.8 \cdot 10^{-24}$ cm²) hyperfine structure.

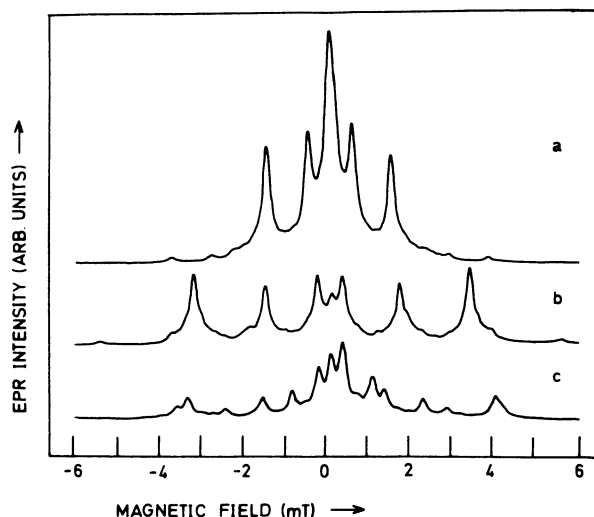


Figure 1. EPR spectra of ¹⁰⁵Pd (93.8 % enrichment) for defects with the 2-fold axis in the (011)-plane. a: $\vec{B} \parallel \langle 100 \rangle$, b,c: $\parallel \langle 011 \rangle$.

We diffused natural and enriched (93.8% ^{105}Pd) palladium into n(P) type crystals of 1 Ωcm room temperature resistivity. The treatment took 16 hours at 1200 °C and was followed by quenching in water. The EPR intensity improved if palladium and iron were diffused together. Codoping with iron enriched up to 95% ^{57}Fe did not result in any splitting or broadening of the $\text{Si}:\text{Pd}^-$ spectrum. Therefore, this interesting effect may not be taken as evidence for the incorporation of iron in $\text{Si}:\text{Pd}^-$.

The EPR spectrum (see figure 1) has an involved hyperfine structure with line crossings. The line intensities are angular dependent and for some magnetic field directions forbidden lines appear. The nuclear interactions influence the allowed transitions only through higher order mixing of quadrupole and hyperfine effect [6]. The forbidden transitions show first order effects. This allows a good determination of the quadrupole effect from EPR.

^{105}Pd ENDOR was observed over a range of frequencies from 0 to 55 MHz. The ENDOR intensity was angular dependent, being strongest in the $\langle 100 \rangle$ direction. An example of an angular pattern for the defect orientations with the two-fold axis in the $(0\bar{1}1)$ -plane is shown in figure 2. The splitting in two curves is a result of the Zeeman interaction with the ^{105}Pd nucleus, which has $g_N\mu_N/h=1.97$ MHz/T [7]. From the fact that the patterns cross the nuclear g-tensor can be seen to be very anisotropic in this case. This is remarkable, as $\vec{g}_N$ is usually purely isotropic. Both the EPR and the ENDOR spectrum can be described with the spin hamiltonian

$$H = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} - \mu_N \vec{B} \cdot \vec{g}_N \cdot \vec{I} + \vec{S} \cdot \vec{A} \cdot \vec{I} + \vec{I} \cdot \vec{Q} \cdot \vec{I}, \quad (2)$$

with $S=1/2$ and $I=5/2$. For the parameter values, given in table 1, the experimental and theoretical line positions never differed by more than 20 kHz c.q. 20 μT . Also the line intensities are correctly predicted. A computer fit to the ENDOR data was not possible for $\vec{g}_N$ fixed to the literature value.

Table 1. Spin hamiltonian parameters of $\text{Si}:\text{Pd}^-$

interaction	tensor	zz	xx	xy	unit
electronic Zeeman	g	2.05510(4)	1.94531(4)	0.02628(2)	
nuclear Zeeman	g_N	-1.965	0.094	2.011	MHz/T
hyperfine	A	19.279	35.558	-0.448	MHz
quadrupole	Q	-12.795	6.3975	-9.446	MHz

The anisotropy of $\vec{g}_N$ cannot be explained within the vacancy model. Notably, the ^{17}O ENDOR of $\text{Si}:\text{OV}^-$ [8] could be described using an isotropic nuclear g-value close to the literature value. A likely explanation is the mixing of nuclear spin with orbital moment through orbital hyperfine interaction. Such an effect is similar to the spin-orbit mixing resulting in electronic g-shifts. Although a quantitative analysis is required, it seems safe to conclude that orbital momentum is present and that the Pd atom is in an open shell configuration. In the conventional LCAO analysis [9], using the value $A_C=1460$ MHz and $P_d=188$ MHz [10], the hyperfine interaction yields 2.1% s- and 10.1% d-electron localization on the Pd site. The observed quadrupole interaction, on the other hand, would require some 50% d-electron charge at the Pd site. Therefore, a highly non-tetrahedral valence charge distribution must also be present. Contrary to the vacancy model, the dihedral model provides just such a valence charge distribution.

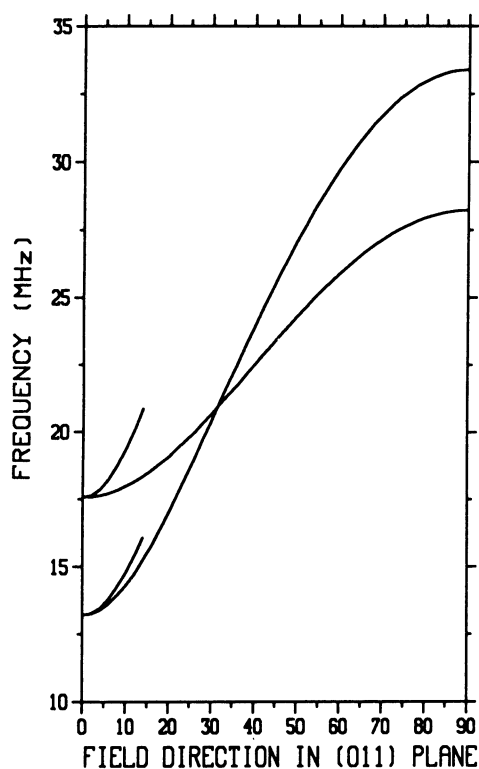


Figure 2. ^{105}Pd ENDOR for defects with the twofold axis in the $(0\bar{1}1)$ -plane.

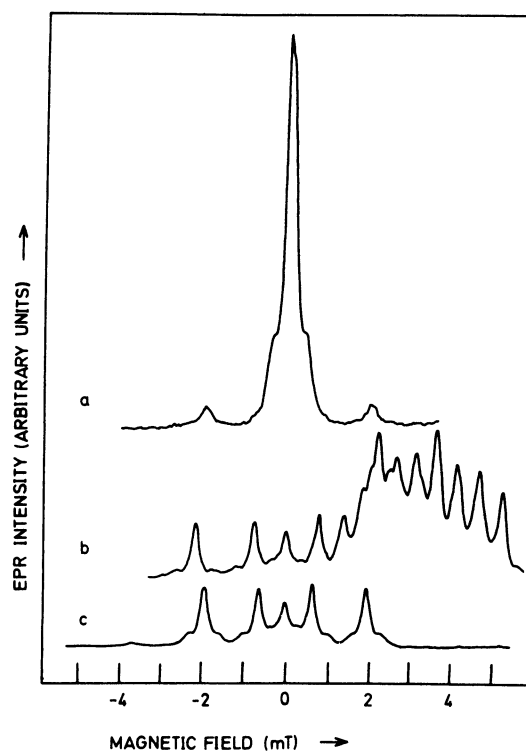


Figure 3. EPR spectrum of $\text{Si:}^{61}\text{Ni}^-$ (88.1 %) for defects with the twofold axis in the $(0\bar{1}1)$ -plane. a: $\vec{B} // \langle 100 \rangle$, b,c: $\vec{B} // \langle 011 \rangle$.

EPR OF $\text{Si:}^{61}\text{Ni}^-$

EPR studies were made on Si doped with nickel enriched to 88.1% ^{61}Ni . The silicon starting material was of n(P) type with 8 Ωcm room temperature resistivity. The diffusion was performed at 1200 $^{\circ}\text{C}$ during 16 hours and followed by quenching in water. The EPR spectrum (figure 3) showed fourfold splitting, proving the presence of a ^{61}Ni nucleus ($I=3/2$) in the center. The resulting parameters are shown in table 2, with the parameters of $\text{Ge:}^{61}\text{Ni}^-$ from reference [1]. The data show that the two centers have the same structure.

Table 2. Spin hamiltonian parameters of $\text{Si:}^{61}\text{Ni}^-$ and $\text{Ge:}^{61}\text{Ni}^-$ [1]

center	tensor	zz	xx	xy	unit
$\text{Si:}^{61}\text{Ni}^-$	g	2.0163	2.0359	0.0177	
	g_N	2.5	~ 1.4	-3.7	MHz/T
	A	-1.0	38.8	-1.2	MHz
	Q	-2.4	1.2	3.3	MHz
$\text{Ge:}^{61}\text{Ni}^-$	g	2.0294	2.0651	0.0475	
	A	≤ 4.8	33.8	-2.9	MHz

The EPR fit significantly improved when the anisotropic $\vec{g}_N$ from table 2 was substituted for the isotropic value of 3.81 MHz/T [7]. The hyperfine interaction has similar features as for the case of Si: $^{105}\text{Pd}^-$. With $A_c=2499$ MHz and $P_d=376$ MHz [10], one finds 1.0% s- and 12.4% d-electron localization on the Ni atom. The quadrupole effect would require a d-electron localization of ca. 16%, indicating a smaller valence charge imbalance than was found for Si: $^{105}\text{Pd}^-$. Again the experimental data provide support for the dihedral model over the vacancy model.

EPR IDENTIFICATION OF PtFe AND PdFe

Platinum diffusion was carried out under the same conditions as for palladium. Without codiffusion of iron, only the EPR spectrum of Si:Pt $^-$ was observed. If iron was codiffused, the Si:Pt $^-$ spectrum was no longer present, but instead strong EPR due to the trigonal Pt(II) center was observed. This center was speculated to be oxygen related [2]. The spectrum showed the large hyperfine satellites due to interaction with the 33.7% abundant ^{195}Pt nucleus ($I=1/2$). Upon codiffusion with iron enriched to 95% ^{57}Fe , a well resolved splitting was observed, proving the presence of a single ^{57}Fe nucleus ($I=1/2$) in the center. A similar trigonal spectrum was observed in palladium diffused crystals. It showed an analogous ^{57}Fe hyperfine splitting. Due to the low intensity, the complicated ^{105}Pd ($I=5/2$) hyperfine structure could not be analyzed. Both centers have very similar parameters (see table 3) and are most likely nearest neighbor pairs. A simple LCAO analysis yields 22.3% d-electron localization on the Pt and 21.5% on the Fe site, indicating that both atoms are paramagnetic.

Table 3. Spin hamiltonian parameters of Si:PtFe $^-$ and Si:PdFe $^-$

tensor	$^{195}\text{Pt}^{57}\text{Fe}^-$		$\text{Pd}^{57}\text{Fe}^-$		unit
	xx	xy	xx	xy	
g	2.0884	-0.0380	2.0727	-0.0160	
A	280	94			MHz
A- ^{57}Fe	6.3	6.0	~6	~6	MHz

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