

## L-edge x-ray absorption resonances in palladium silicides and palladium metal

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The Pd  $L_{2,3}$  white line absorption has been measured for Pd metal, Pd<sub>2</sub>Si, and PdSi to probe the variations in occupation of the Pd  $4d$  states due to the rehybridization of the  $d$  band in the silicides. A reduction of the density of occupied states of  $d$  character in Pd<sub>2</sub>Si and PdSi with respect to Pd metal is found, in agreement with partial-density-of-states calculations for the hybrid-bonded silicides.

The  $L_2$  and  $L_3$  absorption edges of many solids are characterized by the presence of pronounced resonances, "white lines" (WL), near the absorption threshold. For a variety of transition metals, it has been shown that the dominant cause for these WL's are dipole-allowed transitions to final states of proper symmetry above the Fermi level ( $E_F$ ) (unoccupied in the ground-state metal).<sup>1</sup> Since the  $2p$  core states of transition metals maintain their atomic symmetry almost unperturbed,<sup>2</sup> the  $L_{2,3}$  absorption probes the density of final states of  $s$  or  $d$  character.<sup>3</sup> The transition to  $s$  final states produces a smooth onset of the absorption above threshold due to the delocalized nature of the  $s$  states and the small dipole oscillator strength for such transitions. An example of absorption to  $s$  states is given by Ag, the noble element following Pd in the  $4d$  period, where no  $4d$  final states are available. Hence, no white line is observed above the  $L_2$  and  $L_3$  edges.<sup>4,5</sup> Transitions to final states of  $d$  character, when allowed, can result in sharp white lines. Thus the intensity of the  $L_{2,3}$  absorption white lines will be sensitive to variations of the  $d$  component of the density of empty states above the Fermi level.<sup>6</sup> The formation of chemical bonds between transition metals and  $s$ - $p$  valence elements affects the occupancy and/or hybridization of the  $d$  states, and this change can be revealed in the white line intensities.

Recently, Lytle *et al.*<sup>7</sup> have demonstrated an inverse correlation between the intensity of the  $L_3$  edge resonance and the  $d$  occupancy for Pt, Ir, and Au.  $X\alpha$ - $sw$  cluster calculations by Horsley<sup>8</sup> yielded a linear relationship between the density of unoccupied  $d$  states and the sum of the intensities (peak areas) of the  $L_2$  and  $L_3$  edge resonance lines for several Pt compounds. In addition, the ratio of the  $L_3$  and  $L_2$  edge resonances reflects the relative occupancy of the

$d_{3/2}$  and  $d_{5/2}$  subbands because the electric dipole selection rule couples only initial and final states with  $\Delta j = 0, \pm 1$ . The white line (WL) intensities at the  $L_2$  and  $L_3$  edge of Pt metal were found<sup>1</sup> to differ by a factor of 14 ( $L_3/L_2 \cong 14$ ), which indicates that the empty part of the  $5d$  band (0.3 states per atom) belongs almost entirely to the  $5d_{5/2}$  subband.

Brown *et al.*<sup>1</sup> substantiated this observation with a tight-binding calculation of the  $5d$  band of Pt. In Pd metal, whose  $4d$  occupancy was established by Vuillemin<sup>9</sup> to be 9.64 and 0.36 empty  $d$  states per atom, Sham<sup>4</sup> observed strong  $L_{2,3}$  white lines with a  $L_3/L_2$  ratio of 2.6, indicating a smaller  $d_{5/2}$  subband dominance than in Pt. In the present paper, we show that the intensity of the  $L_2$  and  $L_3$  absorption edge resonances can be utilized for the characterization of transition-metal compounds where rehybridization of the valence  $d$  states occurs.

Typical cases of hybrid  $d$ - $p$  valence bands are found in the transition-metal silicides<sup>10</sup> where Si  $p$  and metal  $d$  orbitals form bonding and antibonding partially occupied states. This description of the electronic structure of transition-metal silicides was obtained on the basis of photoemission,<sup>11</sup> Cooper minimum photoemission,<sup>12,13</sup> Auger line-shape analysis,<sup>11,14</sup> and photoionization cross-section measurements<sup>15</sup> for the near-noble-metal silicides, and was then confirmed by total and partial density-of-states (DOS) calculations.<sup>16,17</sup> In particular, the Pd silicides' Pd<sub>2</sub>Si and PdSi electronic structure is well understood in terms of Si  $3p$ -Pd  $4d$  hybrid bonding states at  $\sim -3$  eV below  $E_F$  and partially occupied antibonding states in the  $E_F$  region.<sup>11-17</sup> The total occupation number of these  $d$ -dominated hybrids has been a controversial factor, though, whose determination had to rely upon calculated DOS, since none of the surface-sensitive spectroscopies used in the study of Pd<sub>2</sub>Si and PdSi

yield information on this crucial point.

Here we present measurements of the  $L_2$  and  $L_3$  white line intensities for bulk, and *in situ* prepared,  $Pd_2Si$  and  $PdSi$  using monochromatic synchrotron radiation. The experiment was carried out on the double-crystal UHV monochromator "Jumbo" at Stanford Synchrotron Radiation Laboratory (SSRL) by detecting the total electron yield (TY) and the Auger yield (AY) emitted as a consequence of the  $L$ -edge x-ray absorption.<sup>5,18</sup>

The Pd sample was obtained by evaporating a thick ( $\sim 300$ -Å) Pd film *in situ* (base pressure  $8 \times 10^{-11}$  torr) onto a stainless-steel substrate. The bulk  $Pd_2Si$  and  $PdSi$  samples labeled A and B had been prepared *ex situ*<sup>19</sup> by reacting a thick ( $\sim 500$ -Å) Pd layer deposited onto a Si (111) substrate to 200 °C for 30 min and to 800 °C for 30 min, respectively.<sup>20</sup> The  $Pd_2Si$  preparation is known to give a slightly underreacted silicide where the top layers of material were still Pd rich as a residual of the not fully consumed Pd film.<sup>20</sup> Other samples were prepared *in situ* by evaporating in UHV a thin layer of Pd,  $\sim 50$  Å, and heating to 520 °C for 25 min to form  $Pd_2Si$  (sample C) and to 800 °C for 30 min to form  $PdSi$  (sample D). It has been established<sup>21,22</sup> that, for such preparation procedures, Si segregation takes place and that a Si-rich surface is obtained. These considerations are of importance since our measurement technique is also sensitive to the top layers. Figure 1 shows the  $L$  absorption spectra for Pd and  $Pd_2Si$  (sample A), and Fig. 2 gives the details of the change in the  $L_3$  (most intense) WL.

The variations of the total  $L_2$  plus  $L_3$  WL intensities for the silicides defined with respect to the smooth atomiclike absorption at 30 eV above threshold are summarized and compared to metallic Pd in

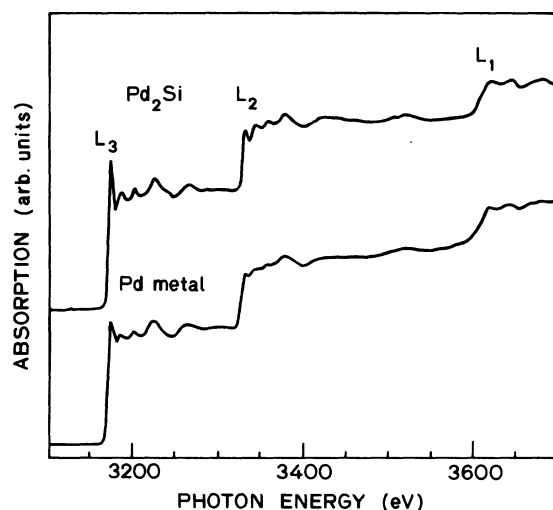


FIG. 1.  $L$ -shell absorption spectra for Pd metal and  $Pd_2Si$  (sample A).

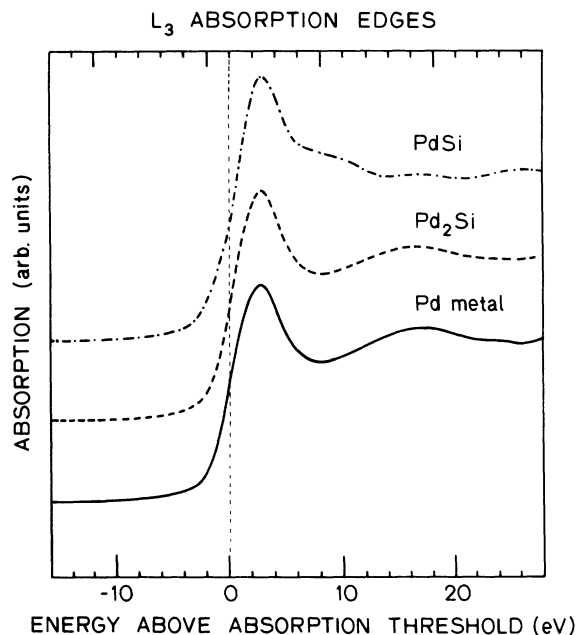


FIG. 2.  $L_3$ -edge white lines for Pd metal,  $Pd_2Si$ , and  $PdSi$ . The WL intensity has been measured with respect to the absorption intensity at  $\sim 30$  eV above threshold.

Table I. There is a monotonic increase of the white line intensities from Pd to  $Pd_2Si$  to  $PdSi$  which indicates an increase of empty  $d$  final-state density. Thus the occupation of the valence states of  $d$  character in the silicides decreases with the increase of the Si concentration. The differences between the values obtained for the bulk silicides and the *in situ* prepared  $Pd_2Si$  and  $PdSi$  will be discussed below.

The increase of the unoccupied  $d$  states in the silicides is in excellent agreement with the DOS calcula-

TABLE I. Total white line intensities (relative to the atomic absorption  $\sim 30$  eV above the edge) ( $L_2$  plus  $L_3$ ) for  $Pd_xSi$  and Pd.

	Experiment (%)	Theory (%)
Pd	0	0
$Pd_2Si$ A <sup>a</sup>	+6	+10
$PdSi$ B <sup>b</sup>	+30	+35
$Pd_2Si$ C <sup>c</sup>	+30	
$PdSi$ D <sup>d</sup>	+35	

<sup>a</sup>  $\sim 500$ -Å Pd heated to 200 °C for 30 min.

<sup>b</sup>  $\sim 500$ -Å Pd heated to 800 °C for 30 min.

<sup>c</sup> 50-Å Pd heated to 520 °C for 25 min.

<sup>d</sup> 50-Å Pd heated to 800 °C for 30 min.

tions by Bisi and Calandra.<sup>16,23</sup> The calculated occupation numbers for the  $d$  partial DOS in the silicide valence band give a 10% increase of the number of  $d$  holes in going from Pd to Pd<sub>2</sub>Si and an increase of 35% from Pd to PdSi.<sup>23</sup> This calculation was done with a semiempirical extended Hückel method and is described in Ref. 16. The absolute occupation number for Pd is 9.08, which is different from what was obtained by Vuillemin.<sup>9</sup> The Hückel method guarantees, however, that the relative changes are genuine. It is these relative changes which are also the most reliable quantities extracted from our data since an absolute quantification of the white line intensities would encounter large difficulties, at present, due to a lack of knowledge of the inherent line shapes and absolute cross sections for absorption.

The quantitative discrepancy between our measurements and the theoretical prediction is satisfactorily explained considering the nature of our samples and the surface sensitivity of our measurements. As mentioned above, the bulk Pd<sub>2</sub>Si sample A had a not fully reacted layer of Pd at the surface due to the sample preparation method. The white line measured for this sample is therefore referred to a Pd-rich average composition and not to uniformly stoichiometric Pd<sub>2</sub>Si. The smaller deviation measured in the WL intensity (+6%) is therefore understood.

A symmetric argument is appropriate for explaining the results on the *in situ* prepared thin Pd<sub>2</sub>Si film (sample C). As already noted, a Si-rich layer is formed at the surface, corresponding to a more dilute silicide with respect to the bulk. The +30% measured increase of the WL indicates that the top layers of the *in situ* reacted Pd<sub>2</sub>Si had an average composition close to PdSi, i.e., the Pd in the top layers was mostly coordinated with Si atoms, as is expected in a Si-rich region, and had a bonding configuration closer to PdSi than to Pd<sub>2</sub>Si. Because of the thinness of the Pd<sub>2</sub>Si film, the surface layers are expected to yield a significant contribution to the measured signal. The same segregation effect could also be present, to a lesser extent, in the *in situ* prepared thin PdSi sample D which would yield a higher surface to bulk PdSi contribution than the thicker PdSi sample B.

The analysis of the partial  $L_2$  and  $L_3$  intensities is summarized in Table II where the  $L_3/L_2$  ratio is given for the samples. The ratio decreases from 2.75

TABLE II. White line intensity ratio  $L_3/L_2(4d_{5/2}/4d_{3/2})$ .

Pd	2.75
Pd <sub>2</sub> Si A <sup>a</sup>	2.57
PdSi B <sup>b</sup>	2.2
Pd <sub>2</sub> Si C <sup>c</sup>	2.32
PdSi D <sup>d</sup>	1.96

<sup>a</sup> ~ 500-Å Pd heated to 200 °C for 30 min.

<sup>b</sup> ~ 500-Å Pd heated to 800 °C for 30 min.

<sup>c</sup> 50-Å Pd heated to 520 °C for 25 min.

<sup>d</sup> 50-Å Pd heated to 800 °C for 30 min.

for Pd metal<sup>24</sup> to ~ 2.5 to 2.3 for Pd<sub>2</sub>Si to practically the atomic statistical ratio of 2 in PdSi. This trend of the atomiclike distribution between the spin-orbit components of the increased fractional  $d$  hole with the dilution of Pd in Si is worth mentioning because it can stimulate some theoretical work on the mixing of spin-orbit components of hybrid  $d$  bands in solids.<sup>25</sup>

We conclude that absorption edge measurements of the  $L_{2,3}$  white lines carry direct information on the variations of density of states in the  $d$  valence band of transition-metal compounds. In particular, we have shown that the  $4d$  states in Pd<sub>2</sub>Si and PdSi are occupied to a smaller degree than in Pd. This definitely disproves the early theoretical "noble-metal-like" models for the DOS of Pd silicides and strongly confirms the hybrid orbital explanation reflected in the calculations by Bisi and Calandra.<sup>15</sup> The high sensitivity of our measurements to the surface composition of the samples indicates the applicability of this approach to interface studies.

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<sup>6</sup>Changes in the many-body interactions that determine the x-ray absorption resonance line shape (Ref. 1) going from Pd to the Pd silicides are expected to be of small importance with respect to the main cause of the WL (dipole

- transition from  $2p$  to  $4d$  states). Furthermore, our method of normalizing the WL intensities of  $\text{Pd}_2\text{Si}$  and  $\text{PdSi}$  to the measured intensity for metallic Pd further reduces the weight of line-shape effects that practically cancel out. This is true because of the permanence of the metallic character in all the solids measured in the study.
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