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Near-edge x-ray-absorption fine-structure spectroscopy measurement of the p -symmetry unoccupied states of silver, palladium, and palladium silicide

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(Received 27 November 1989)

The density of unoccupied p states of silver, palladium, and palladium silicide has been measured for the first time with high resolution by x-ray absorption at the $M_{IV,V}$ edges. Our results show that the $M_{IV,V}$ -edge spectra yield information for $4d$ metals similar to that provided by K and L_I edge measurement on $3d$ metals. The densities of states are in agreement with theoretical predictions both in regard to energy and relative intensity. Changes in the palladium $M_{IV,V}$ spectra on silicide formation give the first direct evidence of the role of Pd $5p$ states in compound formation.

X-ray-absorption spectroscopy at the K and L edges has been used for many years to probe the density of states above the Fermi level.¹ The optical selection rules $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$ allow the determination of l - and j -projected densities of states. For light elements, K -edge spectra provide a precise measurement of the density of unoccupied p states because the K -hole lifetime broadening is small. For heavier elements, such as the $4d$ elements, this lifetime broadening is large (~ 6 eV, Ref. 2) so that K -edge measurements are restricted to $3d$ metals and lighter elements. The L_I edge is also broad (~ 6 eV), so it is not possible to measure the density of p states with high resolution at this edge either. The L_{II} and L_{III} edges are relatively sharp (2.1 eV) and much useful information has been obtained about the density of d states in palladium silicide and palladium by measuring the near-edge spectra at these edges,³⁻⁵ but no information is provided about the density of p states, which also determine some material properties. For a high-resolution determination of the density of unoccupied p states of a $4d$ metal or compound, a core state with long hole lifetime, such as the $3d$ level, must be used. Transitions from the $3d$ level ($M_{IV,V}$ edges) to unoccupied p and f states are sharp (~ 0.4 and 0.3 eV, Ref. 6) and allowed, but until now no high-resolution measurements at threshold have been carried out. It is generally believed that the f states dominate the spectra, because the $\Delta l = 1$ ($d \rightarrow f$) transitions are about

100 times more intense than $\Delta l = -1$ ($d \rightarrow p$) transitions.⁷ However, since the $4f$ states of $4d$ metals are well above the Fermi level, the edge spectra at onset should correspond substantially to the unoccupied density of p states.

Although this procedure seems simple enough, there appear to be no reports in the literature of such threshold measurements and there are two reasons for this. First, as stated above, the $\Delta l = -1$ transition is roughly 2 orders of magnitude weaker than the $\Delta l = +1$ and most of the oscillator strength is in the $d \rightarrow f$ transition ($\Delta l = +1$). This low signal intensity means that a sensitive measurement system is required. Second, the $M_{IV,V}$ edges of $4d$ metals typically lie between 150 and 400 eV, a part of the electromagnetic spectrum where it has traditionally been difficult to obtain both high flux and high resolution over a wide spectral range.⁸ Each experiment requires a particular combination of flux and resolution. Our results were obtained with the aid of synchrotron radiation and a new x-ray monochromator (High-Energy Toroidal Grating Monochromator 2, Ref. 9) at the Berlin Storage Ring BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung). We show that the determination of the density of p states with high-resolution x-ray absorption is not restricted to light elements such as C, O, and the $3d$ metals. The density of unoccupied p states of $4d$ metals can be measured at the $M_{IV,V}$ edges to provide

similar information to K -absorption spectra of light elements. This represents a very substantial extension of the number of systems which can be studied with high-resolution near-edge x-ray-absorption fine-structure spectroscopy (NEXAFS).

Palladium and silver were prepared by evaporation of 300 Å of the metal onto a stainless-steel substrate in a vacuum of 3×10^{-10} mbar. Palladium silicide was prepared as a thin film on a Si(111) substrate. The Si(111) crystal was chemically cleaned,¹⁰ mounted in the vacuum chamber, and heated to 1200 K to produce a clean, (7×7) reconstructed surface. 40 Å of palladium were evaporated onto the surface and then it was heated to 650 K to produce a fully reacted silicide film.¹¹ Absorption was measured as total electron yield from the sample.¹² The spectra were then divided by the total electron yield from a freshly evaporated gold diode in order to normalize out the transmission of the monochromator. Since we are dealing with weak signals, we checked for possible spurious structures which could come from the normalization, due for example, to the Au $N_{IV,V}$ edge. This was done by normalizing to a silicon diode instead of gold; the spectra were not materially altered. Finally, all spectra were divided by the value of the pre-edge minimum to allow direct comparison of the spectra of different materials.

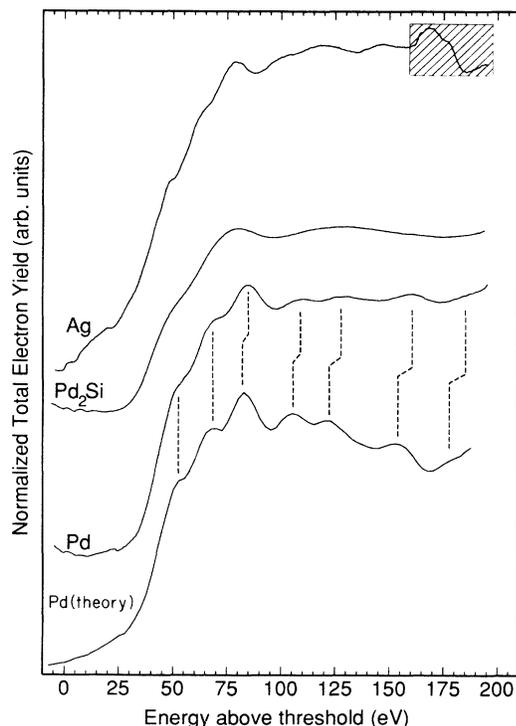


FIG. 1. Broad scan x-ray-absorption spectra of Ag, Pd₂Si, and Pd at the $M_{IV,V}$ edges, together with a theoretical simulation for Pd (Ref. 14). The calculated spectrum has been shifted 2.6 eV to higher energy, in order to best align the EXAFS structure. The structures in the shaded region are due to oxygen contamination of the monochromator. A slight distortion is evident in the prethreshold region; this arises from the different beam lifetimes during measurement of the spectrum and the normalization curves.

From the long-range scans, the ratio of the Pd₂Si and Pd edge jumps was determined to be 0.69, consistent with the fact that Pd atoms in Pd₂Si are less dense by a factor of about 0.7 with respect to pure Pd.³

Figure 1 shows wide scans above the $M_{IV,V}$ edges of Pd, Ag, and Pd₂Si, compared with the calculations for Pd of Müller and co-workers.^{13,14} These broad scans are indeed dominated by the f -like states well above threshold. The structure in the Pd spectrum is, in general, less pronounced than in the calculations but the overall agreement is excellent. The small energy-dependent shift in the position of the structures can be explained in terms of self-energy corrections.¹⁵ The fine structure of the Pd and Ag spectra are rather similar, as expected from their closely related electronic and crystallographic structure, but for Ag it is compressed in reciprocal space, relative to Pd, because the lattice parameter is larger in real space. The Pd₂Si spectrum shows the same large rise in cross section due to f -symmetry final states (an atomic effect) but very different fine structure (solid-state effect).

In Fig. 2 some details are shown of the absorption spectra close to threshold together with the calculated spectra.

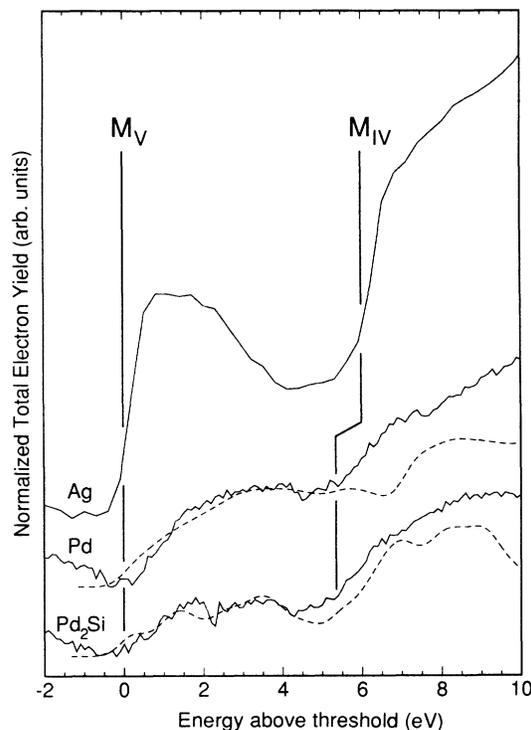


FIG. 2. Near-edge x-ray-absorption spectra at the $M_{IV,V}$ edges of Ag, Pd, and Pd₂Si. The onsets of the M_V edges have been aligned using the core-level shift between Pd and Pd₂Si (Ref. 16). Onset energies are Pd₂Si, 336.8 eV; Pd, 335.2 eV; Ag, 368 eV; absolute accuracy ± 1 eV. Theoretical curves were obtained by broadening the theoretical density of p -symmetry states by the experimental resolution, and adding a spectrum shifted by the spin-orbit splitting and weighted by the branching ratio, to take account of both the M_{IV} and M_V edges. The theoretical Pd curve has been normalized at the experimental height, while the ratio between the Pd₂Si and Pd theoretical curves is 0.7, as expected from the Pd atomic density ratio.

In the single-particle picture the p contribution to the M absorption spectrum is given by the p -projected density of states (p -PDOS) modulated by the matrix element of the transition between d core states and p empty states. The energy dependence of this matrix element is weak and its effect is simply to increase the relative weight of the higher-energy states.⁵ Thus a direct comparison between the measured absorption and the calculated PDOS is a reasonable approximation and the measured $M_{IV,V}$ NEXAFS spectra provide directly the main features of the p -PDOS. The Pd and Pd₂Si electron states were evaluated by the linear muffin-tin orbital, atomic sphere approximation (LMTO-ASA) method as described in detail in Ref. 5. The theoretical absorption spectra are computed by convoluting the theoretical density of p states with the experimental resolution of 0.5 eV, determined from the Ag onset, and adding two statistically weighted spectra separated by the spin-orbit splitting. The resolution is close to the expected value⁹ but it is not possible to extract quantitative data about the relative contributions from the monochromator and lifetime broadening. The M_V edge corresponds to transitions from the $3d_{5/2}$ core state, and the allowed final states are of $p_{3/2}$ character from the $\Delta j = 0, \pm 1$ selection rule. Similarly, at the M_{IV} ($3d_{3/2}$) edge, both $p_{1/2}$ and $p_{3/2}$ final states are allowed, but we expect the $\Delta j = 0$ transitions to be very weak compared with $\Delta j = \pm 1$.¹⁷ The M_{IV} edge therefore samples $p_{1/2}$ final states. The width of the first peak of the density of unoccupied states is ~ 3.5 eV for Ag, in reasonable agreement with the value of 4.2 eV from the calculations quoted in Ref. 1.

The spectrum of Pd is quite different from that of its neighbor in the periodic table, Ag. The onset at the M_V edge is broad, indicating a low density of $p_{3/2}$ states at the Fermi level and a steep rise above it. The silicide absorption spectrum is also quite different from that of Pd metal. This difference is due to the new interaction between Pd and Si present in Pd₂Si. Many experimental and theoretical results show that in this compound the dominant coupling is between Pd $4d$ and Si $3p$ in a bonding-antibonding configuration with the latter dominating the states between the Fermi level and +5 eV (Refs. 5, 18, and 19). Our theoretical calculations suggest that other interactions are present and that near the Fermi level the Si $3p$ and Pd $5p$ coupling is important. As a consequence the Pd $5p$ PDOS is drastically different from that in pure Pd and this difference is still evident after broadening and in the measured spectra which therefore, for the first time, confirms the theoretical prediction of the role of the Pd $5p$

states in compound formation. The shape of the computed curve agrees well with the measured one. This indicates that the single-particle picture is adequate, and that final-state effects, such as the influence of the core hole, are not significant. Note that the relative intensities for Pd and its silicide were not fitted but were directly determined on the basis of the correct density of Pd atoms.

While the agreement between experiment and theory is good at the M_V edge, showing that the measurement directly detects the p -PDOS features, some discrepancies are present at the M_{IV} edge. The spectrum here consists of overlapping structure from the M_{IV} onset and from the M_V spectrum at more than 5 eV above threshold. There are three possible reasons for discrepancies. First, the calculations have not considered spin-orbit effects, and these are likely to lead to differences in the M_{IV} and M_V edges. MacDonald *et al.*²⁰ have estimated a relative shift of about 0.8 eV due to spin-orbit effects for the $p_{1/2}$ and $p_{3/2}$ bands. Second, matrix element effects have also been neglected because they represent a smooth, slowly varying function. Such effects increase in significance away from threshold, so that the calculations of the M_V structure may be less accurate at the M_{IV} edge. Third, the onset of $d \rightarrow f$ transitions may begin to play a role as the energy increases.

In principle, as mentioned earlier, x-ray-absorption spectra at the K or L_1 edge yield the density of $p_{1/2}$ states, i.e., the same information as the M_{IV} spectrum. Insofar as the poorer resolution (lower by an order of magnitude) of the K and L_1 spectra allows a comparison, these previous results are consistent with the present results. Sham,¹ Müller *et al.*,² and De Crescenzi *et al.*²¹ have reported the spectra for Pd, Ag, and Pd₂Si. Sham noted "slightly different" features for Pd and Ag, which are much more evident in the $M_{IV,V}$ spectra.

In summary, we have shown that j -projected density of unoccupied p states can be determined with high resolution at the $M_{IV,V}$ edges. The results are in satisfactory agreement with calculations. For light elements, it is sufficient to measure the l -projected density of states at the K and L_1 edges to obtain the density of unoccupied p states. Spin-orbit splitting is not important and resolution is good. For $4d$ metals, lifetime broadening severely reduces the resolution at the K and L_1 edges. $M_{IV,V}$ -edge absorption then provides the required information with high resolution and the added advantage that spin-orbit effects may be observed as differences between the M_{IV} and M_V edges.

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