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$M_{4,5}N_{4,5}N_{4,5}$ Auger-electron spectrum of free Pd atoms

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The $M_{4,5}N_{4,5}N_{4,5}$ Auger-electron spectrum of free palladium atoms has been measured by means of a new high-temperature spectrometer using electron-beam excitation. The experimental spectrum has been compared with the theoretical profile calculated in a nonrelativistic mixed-coupling scheme applying *jj* coupling to the initial state and intermediate coupling to the final one. The energies have also been compared with the theoretical results obtained from relativistic intermediate-coupling calculations. Apart from the Auger energies, the free-atom $3d$ binding energies $E_B(3d_{5/2})=341.13(15)$ eV and $E_B(3d_{3/2})=346.45(15)$ eV have also been determined with the aid of optically known two-hole final-state energies. Comparisons with the solid-state photoelectron and Auger-electron measurements give free-atom–metal shifts of 1.3 eV for the 3d binding energies and 11.3 eV for the $M_{4,5}N_{4,5}N_{4,5}(^1G_4)$ Auger energies, also referring the solid-state energies to the vacuum level.

INTRODUCTION

Palladium provides an interesting object for vapor-phase Auger measurements for several reasons. It has a closed $4d$ subshell electronic structure in its ground state, and hence the open-shell structure observed in the spectrum is all due to the Auger decay. Since the double-hole final-state energy levels are known optically,[1] they can be used as the starting values in the fitting of the experimental $3d^{-1}\rightarrow 4d^{-2}$ Auger spectrum. This makes possible an accurate determination of the line intensities and a reliable comparison between the experimental and calculated profiles. On the other hand, a comparison of the experimental values with the energy splittings calculated nonrelativistically and relativistically in the intermediate coupling at this medium-Z value serves as a test for the accuracy of the widely used nonrelativistic intermediate-coupling calculation procedure. Furthermore, the optically known final-state energies can be used to determine the $3d$ binding energies.

Solid-state Auger spectra of Pd have been investigated by several authors in both pure Pd metals and different alloys.[2-7] The spectra have been found to be highly sensitive to the composition of the sample. Very broad bandlike features have been observed in, e.g., pure Pd surfaces, whereas narrow spectral features are found[2] in $Mg_{75}Pd_{25}$, approaching atomiclike structure. Also, for a reliable interpretation of these solid-state effects, it is very important to know the true atomic Auger spectrum of free Pd atoms.

Free-atom–metal shifts in the binding and Auger energies are of particular interest for Pd, because the screening mechanism changes when the $4d$ shell becomes completely filled. Apart from the $M_{4,5}N_{4,5}N_{4,5}$ Auger energies, the free-atom–metal shifts can also be determined for the $3d$ binding energies with the aid of optical values.

EXPERIMENTAL

The Auger spectra have been measured by means of the new high-temperature spectrometer system.[8] The spectrometer consists of a double-pass simulated spherical-type[9] analyzer with a four-element preretardation lens.[10] The mean radius of the analyzer is 65 mm and the length of the lens 250 mm. The sample is heated by the inductive heating method, applying an rf generator with a 200-kHz operating frequency and a maximum 3-kW output power. The spectrometer is shown schematically in Fig. 1.

The spectra have been measured with use of a microprocessor to control[11] the retardation voltage and the voltages of the different lens elements as well as to collect the data. The pass energy of the analyzer was kept at a constant value of 50 eV. No direct temperature measurement was made but the temperature was estimated to be around 1600 K. The Pd atoms were ionized by a primary beam of about 1-mA current and 3-kV voltage going through the graphite furnace.

The final experimental spectrum, formed as a sum of several short runs, is shown in Fig. 2. The energy calibration was performed with the aid of Ar $L_3M_{2,3}M_{2,3}(^1D_2)$ and Ne $KL_{2,3}L_{2,3}(^1D_2)$ Auger lines by using for them slightly revised energy values of 203.499(10) eV and 804.458(50) eV, respectively. The value for the Ar Auger line is based on the accurate binding-energy value of 248.629(10) eV of Pettersson *et al.*[12] and King, Trone, Read, and Bradford[13] for the Ar L_3 level combined with the recent optical double-hole–state energy value of 45.127 eV for the $^1D_2$ state from the tables of Bashkin and Stoner[14] and corrected

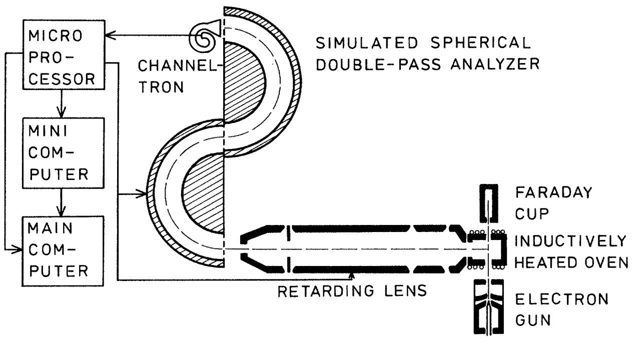

FIG. 1. Schematic of the experimental setup.

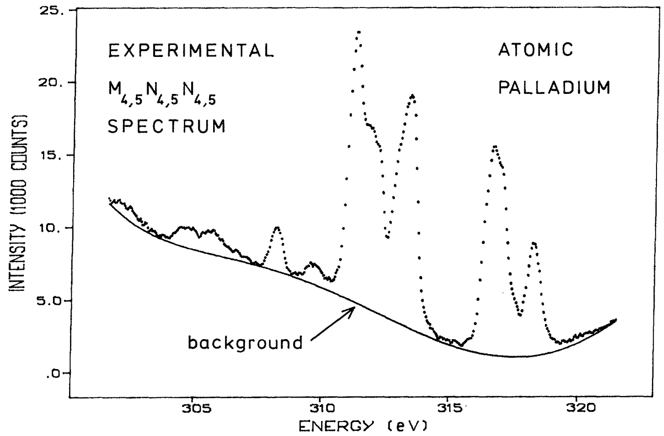

FIG. 2. Experimental $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of Pd. Background shape is shown by solid curve.

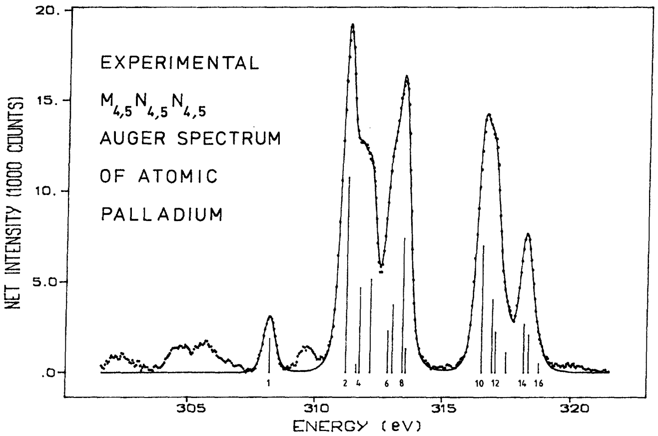

FIG. 3. Separation of the experimental $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of atomic palladium into its components. Solid curve and vertical lines represent a least-squares fit of Voigt functions to the experimental points. The energy separations of the components are taken from the optical data.

for the recoil energy of 0.003 eV. Analogously the value of 804.458 eV for the main Ne Auger line is obtained by subtracting from the binding energy[13] of 870.21(5) eV for the Ne K level the optical final-state energy[14] of 65.730 eV and the recoil energy of 0.022 eV. Principally post-collision interaction[15] causes some shifts for these Auger energies but this effect is to a large extent canceled by the use of nominal reference energy values from soft x-ray and optical spectroscopy for the high excess energies used in these measurments. The adopted value for Ne deviates slightly from the value of 804.557(17) eV given by Thomas and Shaw[16] but its essential advantage is that it has been obtained in a similar way to the Ar value from soft x-ray and optical measurements.

DISCUSSION

The experimental spectrum in Fig. 2 shows increasing intensity at the high-energy end. This is due to the solid Pd condensed partly on the walls of the upper part of the high-temperature oven. The main vapor-phase spectrum resembles in appearance the corresponding spectrum[17,18] of Cd. This was also expected, because the final states $4d^8$ of Pd and $4d^8 5s^2$ of Cd have identical fine-structure energy levels. The larger final-state energy splitting in the case of Cd is reflected in the Auger spectrum as a better-separated fine structure. Towards the lower energies of the main line group the intensity again shows an increasing trend. This is largely caused by the instrumental effects when the analyzer is used in the constant pass energy mode, varying the retardation ratio. This effect was controlled by measuring the Auger spectrum of Ar at the same pass energy. This instrumental part can be represented fairly well by a fifth-order polynomial, and we have therefore subtracted from the experimental spectrum the polynomial background shape shown in Fig. 2 by the solid curve.

The background subtracted spectrum is shown in Fig. 3. In addition to the main diagram lines, some broad structures can be seen on their low-energy side. They can be identified as the $M_{4,5}N$-$N_{4,5}N_{4,5}N$ satellite Auger transitions arising from the primary ionization in the M_1 or $M_{2,3}$ subshells. These primary holes decay very rapidly by the

TABLE I. Experimental and theoretical relative energies (in eV) and intensities (in %) of the $M_{4,5}N_{4,5}N_{4,5}$ Auger lines of palladium.

Assignment of final state	Line number in Fig. 3 M_5	M_4	Energy Experiment (Ref. 1)	Theory Nonrel	Rel	Intensity Experiment M_5	M_4	Theory M_5	M_4
$^1S_0$	1	9	2.98	3.09	3.58	5.2	6.5	3.9	4.1
$^1G_4$	2	10	0.00	0.00	0.00	29.4	33.1	40.9	43.7
$^3P_2$	3	11	0.40	0.40	0.46	1.3	19.1	9.2	11.2
$^3P_0$	4	12	0.53	0.39	0.46	12.9	10.7	0.1	0.0
$^3P_1$	4	12		0.43	0.50			0.1	0.1
$^1D_2$	5	13	0.95	0.87	0.99	14.2	5.4	12.2	16.9
$^3F_2$	6	14	1.63	1.80	2.07	6.4	12.7	8.9	6.3
$^3F_3$	7	15	1.82	1.98	2.27	10.3	10.0	8.9	10.4
$^3F_4$	8	16	2.22	2.32	2.65	20.3	2.5	15.7	7.3

$M_{1,2,3}M_{4,5}N$ Coster-Kronig process, producing double-hole states, which then further decay by the aforesaid satellite Auger transitions to triple-hole states.

The experimental spectrum was decomposed into the line components using a least-squares fitting procedure. For the splitting between the final-state line components, the optically known[1] energy separations were used, and only the line intensities and the absolute energy values were varied with different standard lines. A good fit to the spectrum was obtained with a Voigt profile (full width at half maximum $=0.53$ eV) consisting of the Gaussian and Lorentzian parts with widths of 0.41 and 0.22 eV, respectively. The results are given in Table I and shown in Fig. 3.

The relative energies and intensities of the $3d^{-1} \rightarrow 4d^{-2}$ Auger transitions were calculated in a nonrelativistic mixed-coupling scheme. Numerical values for the Slater integrals were taken from the tables of Mann[19] for the energy calculations and from the tables of McGuire[20] for the intensity calculations. In addition to the nonrelativistic intermediate-coupling energy values, the relativistically calculated values are also given in Table I. Relativistic computations were carried out by the computer code of Grant, McKenzie, and Norrington.[21] The initial- and final-state energy levels were computed separately, and the Auger energies were obtained as their differences.

The theoretical profile shown in Fig. 4 is constructed with the aid of the nonrelativistically calculated relative energies and intensities. A comparison with the experimental profile of Fig. 3 shows a reasonably good agreement between experiment and theory. Relative experimental energies can also be compared with the theoretical values in Table I. Both the nonrelativistic and the relativistic computations seem to overestimate the energy splitting for the doubly ionized atom, which appears to be a common tendency. The nonrelativistically calculated energy splitting is in a slightly better agreement with the experiment than the relativistically calculated energy splitting. This is due to the fact that smaller radial integral values from Mann's tables for the neutral atom are used in the nonrelativistic calculation.

For the $M_{4,5}N_{4,5}N_{4,5}(^1G_4)$ energies the Dirac-Fock calculations gave 313.60 and 318.94 eV, respectively, which values are somewhat larger than the experimental values of 311.16 and 316.48 eV. These calculated values were used in the construction of the absolute energy scale of Fig. 4. Energy regions of the satellite transitions calculated with the Dirac-Fock program are also depicted in Fig. 4.

The free-atom $3d$ binding energies can be determined from the observed Auger energies for $M_5N_{4,5}N_{4,5}(^1G_4)$ of 311.16(15) eV and for $M_4N_{4,5}N_{4,5}(^1G_4)$ of 316.48(15) eV with the aid of 29.97 eV for the Pd III $(^1G_4)$ from Moore's tables.[1] Thus the binding energies $E_B(3d_{5/2}) = 341.13(15)$ eV and $E_B(3d_{3/2}) = 346.45(15)$ eV were obtained. These binding energies were also calculated with the Dirac-Fock program. These calculations gave slightly lower values: 339.94 and 345.28 eV for the $3d_{5/2}$ and $3d_{3/2}$ levels, respectively. The differences between experiment and theory in the absolute binding and Auger energies are mainly due to the fact that the calculations were carried out within a single configuration approximation. The comparatively small deviations, however, indicate that the correlation effects do not play a major role in the case of the $3d^{-1} \rightarrow 4d^{-2}$ transitions of palladium. The experimental $3d_{5/2}$-$3d_{3/2}$ spin-orbit splitting of 5.32 eV is in good agreement with the calculated value of 5.34 eV.

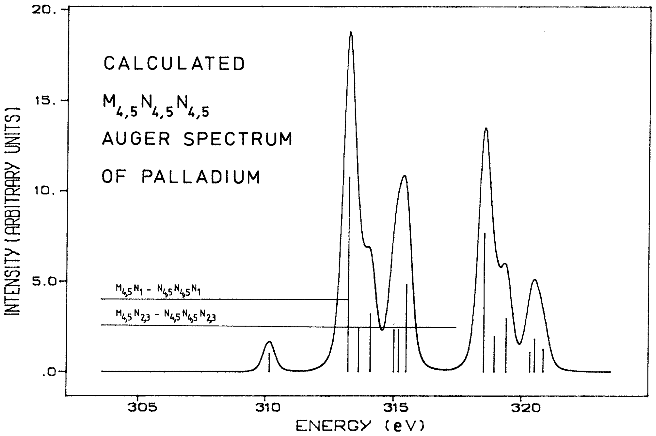

FIG. 4. Theoretical profile of the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions of Pd. Horizontal positions of the bars represent the nonrelativistic energies and their vertical heights the intensities. The linewidth is obtained from the experimental spectrum.

A comparison between the present free-atom binding and Auger energies with the corresponding solid-state values[2,5,22] gives for the free-atom–metal shifts 1.3 eV as the binding energies and 11.3 eV as the Auger energies, when the solid-state values are also referred to the vacuum level, subtracting from the energy difference the work-function value[23] of 5.12 eV. These values compare very well with the semiempirical thermochemical model calculated[24] values 1.5 and 11.4 eV. It should be noted that the determination of the experimental Auger energy shift is not very accurate due to the broad peaks in the solid-state spectrum.

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