Some of the corresponding combinations of singlet terms and of intercombinations between singlet and triplet terms of Pb III have been found by the writer. A more comprehensive account of the spectra of mercury-like atoms will be given at a later date.

In conclusion, the writer wishes to thank Dr. R. J. Lang for the use of his list of wave-lengths and to acknowledge a grant from the National Research Council of Canada.

[Professor H. N. Russell has kindly suggested that an estimate of the ionization potential of Tl+ derived from the difference between the \((6s6s)^1S_0\) and \((6s7s)^1S_0\) terms might be added. On the assumption that these terms follow a simple Rydberg series the lowest \(^1S_0\) term is found to have the value 173350, corresponding to an ionization potential of 21.4 volts. In the case of Hg I a similar calculation gives for the lowest \(^1S_0\) term a value, which is five per cent higher than that obtained from the sharp series of singlets. If a similar error exists for Tl II the ionization potential would be 20.3 volts. This value is rather higher than the estimate of 19.8 volts, which has been made by the writer on the basis of the general progression of term values for mercury-like atoms. The ionization potential of Pb++, it might be added, is approximately 31.3 volts, if it is assumed that the term value of \((6s6f)^3F_4\) of Pb III is 63500.]


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THE INFLUENCE OF THE PRESENCE OF HYDROGEN ON THE \(L_{III}\) X-RAY ABSORPTION EDGE OF PALLADIUM

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It is well known that under suitable conditions palladium will absorb many times its own volume of hydrogen; and the nature of the combination of palladium and hydrogen has been the subject of many investigations. By studying pressure-concentration equilibria of the Pd–H system, it is found that there is an outstanding phase corresponding to a concentration in the neighborhood of 0.5 atom of hydrogen per atom of palladium, suggesting the existence of a compound with the formula Pd₂H₁₆,¹ but the various x-ray investigations of the distension of the palladium lattice due to the absorbed hydrogen are not in complete accord with each other.²⁴⁵ More work dealing with this matter has been done in this
laboratory, and will be reported soon, but the main result is that there exists an outstanding distension \(a_0 = 4.017\) Å of the palladium lattice due to the absorbed hydrogen which is independent of the method used to occlude the hydrogen. Under the same conditions which give the above-mentioned composition, Pd$_3$H, we obtain the value \(a_0 = 4.017\), which, therefore, corresponds to the concentration represented by the formula Pd$_3$H. If these hydrogen atoms are intimately combined with the palladium atoms, it might be expected that the energy values of the palladium atom would be affected, and we have, therefore, studied the \(L_{III}\) absorption edge to see whether changes due to the absorbed hydrogen could be detected.

A Siegbahn vacuum spectrograph was used for this work, and the \(K_1\) and \(K_2\) (1932.30 and 1936.51) lines of iron reflected in the second order from calcite were used as reference lines from which to determine the wavelength of the edges. The dispersion at this position was 20.11 X.U. per mm., the crystal-plate distance being 124.4 mm. The edges were measured on a comparator reading to 0.001 mm. Each plate was measured at from three to eight different points along the edge, and ten readings were taken at each point. It was necessary to roll all of the specimens used to a thickness of 0.001 mm, in order to secure very distinct edges and to bring out their character. With absorbing screens of this thickness, the most dense part of the absorption was confined to a very narrow band, thus giving the appearance of a white line adjacent to the main edge. (See Fig. 1.) Exposures were of the order of 100 milliampere hours.

Hydrogen was occluded in the palladium specimens in two ways. In one method the specimen was made the cathode in dilute H$_2$SO$_4$, platinum being used as the anode. Immediately after electrolysis, the lattice parameter might be greater than \(a_0 = 4.017\), but in the course of ten days or less it would shrink to the value 4.017 and a four-hour x-ray absorption picture would then be taken. Hydrogen was also absorbed from the gas phase. The 4.017 phase obtained in this manner was less stable than the 4.017 phase obtained by electrolysis, completely dissociating in as short a time as eight hours at 20°C. in air, so that it seemed safer to take the absorption pictures while the specimen was in an atmosphere of hydrogen. (This difference in stability has been studied and is to be associated with a difference in the mechanical state of the micro-crystals in the two cases.) It was therefore necessary to put the specimen in a small furnace mounted in place in the vacuum camera. The specimen was heated in vacuo at 200°C. for two hours. Then hydrogen was admitted at one atmosphere pressure and the temperature dropped from 200 to 80°C. in five hours; the temperature was then quickly dropped to 20°C. and a four-hour exposure taken.

The results of these experiments are shown in table 1. It is seen that
Microphotograph of the K absorption edge of Fe.

Microphotograph of the L absorption edge of Fe.

Diagrammatic representation of L absorption edge of Fe.
the wave-length of the main $L_{III}$ absorption edge ($l_1$ in the table) is shifted in the 4.017 phase by 0.87 X.U. (0.6 volt) toward short wave-lengths, and that there is also a second absorption edge, $l_2$, which is 10 X.U. (8 volts) less in wave-length than the pure Pd edge. The second edge, $l_2$, was not dense enough to be measured on the comparator, and the accuracy of these measurements corresponds to about 0.6 volt. This edge, however, is much sharper than is indicated by the microphotogram, figure 4, which enlarges the original plate by 30 times. No difference could be seen between the absorption edges of the electrolytically filled specimens and of the specimens prepared in the hydrogen furnace.

It is well known that x-ray absorption limits of elements are changed by the valency or state of chemical combination of the element, and that in chemical compounds, in addition to the principal edge, there may also be secondary edges or "fine structure." On this basis the results of the x-ray absorption work on the Pd–H system indicate that the hydrogen is in chemical combination with the palladium. There seem to be at least two possible interpretations of the complex absorption edge exhibited by Pd$_2$H. Since there are twice as many Pd atoms as H atoms present, the complex edge might correspond to a Pd atom which shares an H atom with one other Pd atom, or it might correspond to the superposition of two simple edges, one, $l_1$, due to Pd atoms alone, and the other, $l_2$, due to Pd atoms with which are combined H atoms. The relative intensities of the edges are such as to agree with this second hypothesis. An objection to the first hypothesis is that it is unusual to find fine structure caused by chemical combination, and yet the main absorption edge remaining almost unchanged in wave-length, as it does in this case. Chemical combination usually causes a shift of the main edge toward shorter wave-lengths of from 5 to 12 X.U., or more, this shift being larger the greater the valence. To a lesser degree it is also affected by the kind of combining atom.

<table>
<thead>
<tr>
<th>SCREEN</th>
<th>$a_0$</th>
<th>$l_1$</th>
<th>$l_2$</th>
<th>$\Delta l_1$ VOLS</th>
<th>$\Delta l_2$ VOLS</th>
<th>$l_1 - l_2$ VOLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>3.885</td>
<td>3903.90</td>
<td>3903.9</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_2$H</td>
<td>4.017</td>
<td>3903.03</td>
<td>3893.9</td>
<td>3.8</td>
<td>2.4</td>
<td>7.4</td>
</tr>
</tbody>
</table>

On the second hypothesis, the $l_2$ edge is the main absorption edge of a Pd atom with which is combined an H atom; it has been shifted from the position of the pure Pd edge by 10 X.U. toward shorter wave-lengths. The $l_1$ edge is then due to the remaining Pd atoms in the lattice which are not in intimate association with H atoms. The slight shift of this edge (0.87 X.U.) from the pure Pd edge might be due to the greater isolation of the atoms because of the expanded lattice. The available
data on the influence of chemical combination on the position of x-ray absorption edges of elements shows that there is a shift to shorter wavelengths whether the element is electronegative and acquires electrons or whether the element is electropositive and loses electrons in chemical combinations, so that it would be difficult to say whether the palladium atom acquires or loses an electron in the PdH molecule. The recent results of Coehn\(^6\) showing that at least some of the hydrogen is in the ionic state may be of importance in this connection. Further speculation as to the interpretation of the complex absorption edge will probably have to be delayed until there is data on the absorption edges of better known compounds of palladium.

The crystal lattice of Pd\(_2\)H would, on the basis of the second hypothesis, be a face-centered cubic lattice in which alternate grating points are PdH molecules, the remaining points being occupied by Pd atoms. This point of view makes more reasonable the observed fact that much higher concentrations than 0.5 (Pd\(_2\)H) are easily obtained since these higher concentrations would then simply correspond to more of the grating points being occupied by PdH molecules than by Pd atoms. Whereas, if the hydrogen atoms in Pd\(_2\)H were shared between two palladium atoms, then for concentrations higher than 0.5 the excess hydrogen atoms would have to be associated in some different manner.

That the Pd–H system is composed of the units Pd and PdH has been suggested by Linde and Borelius on the basis of experiments on the behavior of the electrical resistance. Oxley\(^7\) has also suggested on the basis of susceptibility measurements that the hydrogen is in intimate association with the palladium. The study of the Pd–H system in this laboratory has been extended in other directions and the results will be reported soon.

In conclusion the writer wishes to express his appreciation to Dr. C. E. Mendenhall for his many valuable suggestions, to Dr. G. D. Van Dyke for the use of the Siegbahn vacuum spectrograph, and to Dr. J. T. Tate of the University of Minnesota for his kindness in making the micro-photograms.

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3 Yamada, Phil. Mag., 45, 241, 1923.
6 A. Coehn, Naturwissenschaften, 11, 183, 1928.

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STUDIES OF THE GALACTIC CENTER. III. THE ABSOLUTE MAGNITUDES OF LONG PERIOD VARIABLES

By Harlow Shapley
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Communicated November 15, 1928

1. That the long period variable stars of spectral class Me are giants at maximum and of intermediate luminosity at minimum has been recognized for many years. That they are closely allied to Cepheid variables in most of their physical properties and therefore that pulsations may be the cause of their variations in light is now also becoming apparent from studies of their spectra, heat indices, and light variations. These variable stars are, however, still something of an enigma. They are widely spread over the sky, they are in the very "earliest" stage of stellar evolution, they have exceedingly low density, and apparently the lowest effective temperatures known.

Among the most uncertain though significant properties of long period