

portant, except in the case of Mn, where the ratio of  $K_\alpha$  for thermal and 0.82-volt neutrons becomes 7.5 instead of the 6.5 for B, thus making still more prominent the resonance in the thermal region.

It must be realized that, while the method outlined in this paper can show, and has shown, resonances in nuclei which are not activated, it

has two drawbacks. One is that, with the few practicable detectors available, the chances are slight that the resonance bands of detectors and absorber will overlap sufficiently for a marked effect, and the other is that, if the absorbing element scatters strongly, the scattering correction is neither unimportant nor accurately calculable.

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## The X-Ray Spectra Arising from the Valence Band— $L$ Transitions of Tungsten, Tungsten Oxide ( $\text{WO}_3$ ) and Platinum\*

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X-ray emission lines and absorption edges arising from transitions between the  $L$  levels and the valence bands of tungsten, tungsten oxide ( $\text{WO}_3$ ) and platinum were studied with a double crystal spectrometer. Manning and Chodorow's calculation of the density of states in the  $5d$  and  $6s$  bands of tungsten is found to be in good agreement with the observed shapes of the tungsten absorption edges. The tungsten emission lines, on the other hand, do not have the structure expected from their calculation and are 4.5 ev narrower than the region of occupied states calculated for these bands. A comparison of the spectra of tungsten metal with those of its oxide shows: (1) the initial

absorption maximum of the  $L_{II}$  and  $L_{III}$  edges is both broader and higher in the oxide, (2) the  $L$  edges of the oxide are shifted 2.5 ev to higher frequencies, (3) the emission lines of the oxide are about 3 ev wider than those of the metal. These differences between the spectra of the oxide and the metal are explained qualitatively in terms of the high electronegativity of oxygen. The platinum absorption edge structures observed are in agreement with what is qualitatively expected from the other properties of this metal. A marked difference in the relative intensity of corresponding structure features of the  $L_{II}$  and  $L_{III}$  edges is ascribed to a spin-orbit coupling of the valence electrons.

### INTRODUCTION

PREVIOUS workers<sup>1-5</sup> have shown that the experimentally observed shapes of x-ray absorption limits and of those emission lines which arise through transitions from the valence bands characteristic of elements in a solid may be interpreted in terms of the density of states in the unfilled and filled portions of these bands. In the present work, the  $L$ -absorption edges and  $L$ -emission lines which involve transitions from the valence bands of tungsten and tungsten

oxide and the  $L$  edges of platinum were studied. The shapes of the tungsten spectra are compared with that of the density-of-states of the  $5d$  and  $6s$  electrons of tungsten calculated by Manning and Chodorow.<sup>6</sup> The  $\text{WO}_3$  and W spectra are compared and their differences explained in terms of the high electronegativity of oxygen. The shapes of the  $L$  edges of platinum are shown to be compatible with band structure expected for this metal from its other properties.

### EXPERIMENTAL

The spectrometer, crystals, high voltage supply and intensity measuring apparatus used in this work have already been described elsewhere.<sup>7</sup> For absorption studies, the target of

\* This research was supported by a grant-in-aid from the American Philosophical Society.

<sup>1</sup> H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

<sup>2</sup> H. Jones, N. F. Mott and H. W. B. Skinner, Phys. Rev. **45**, 379 (1934).

<sup>3</sup> H. Jones and N. F. Mott, Proc. Roy. Soc. **162**, 49 (1937).

<sup>4</sup> A. Sandstrom, Zeits. f. Physik **66**, 784 (1930).

<sup>5</sup> W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

<sup>6</sup> M. Manning and M. Chodorow, Phys. Rev. **56**, 787 (1939).

<sup>7</sup> J. A. Bearden and H. Friedman, Phys. Rev. **58**, 387 (1940).

TABLE I. *Widths of L levels of tungsten.*

	W	Pr	Au
$L_I$	$4.9 \pm 1.0$ ev	$8.0 \pm 1.0$ ev	8.7 ev
$L_{II}$	$3.0 \pm 0.5$	$3.5 \pm 0.5$	3.7
$L_{III}$	$3.4 \pm 0.5$	$3.6 \pm 0.5$	4.4

the x-ray tube was gold plated to give high intensity radiation. The absorbers used in the cases of tungsten and platinum consisted of thin rolled foils. In the case of tungsten oxide, the absorber was prepared by smearing a mixture of powdered  $WO_3$  and thinned Duco cement on onion skin paper. Several layers were used to decrease irregularities in thickness. The remaining inhomogeneities caused only a loss of contrast in the absorption spectra. These absorbers were mounted between the tube and the first crystal on a rotating sector which facilitated moving them in and out of the x-ray beam when comparing direct and absorbed intensities and yet insured the absorbers being returned to the same position in the beam. In some cases, aluminum absorbers of known absorbing power had to be used to reduce the intensity of the radiation below the maximum of 8000 counts per minute allowed by the counting system. These foils were mounted either on the rotating sector or between the first and second crystals.

Because the spectrometer can be reset to 0.1 second, the procedure used was to run through the region of an absorption edge repeatedly in steps of ten or twenty seconds of arc, taking counts of both the direct and absorbed radiation at each point for several minutes. The measurements were corrected for scattered radiation which was taken to be the intensity passed by the spectrometer when the second crystal was turned five to ten degrees away from the Bragg angle. The error in an absorption curve caused by second-order radiation was tested for by repeating a number of points at low voltages. Except in the cases of the  $L_{III}$  edges of W and  $WO_3$ , this correction was found to be less than 6 percent in all cases and was neglected.

In the study of emission lines, the gold was removed from the target. A tungsten button spot-welded onto a nickel backing in hydrogen was soldered on in its place to obtain the tungsten metal lines. To obtain the tungsten lines from the oxide, two different targets were used. The

first was made by pounding the  $WO_3$  into a clean copper surface previously picked full of pockets by a fine steel point. The second was made by pounding it into lead. The two sets of measurements obtained from the two targets agreed well with each other. On exposure to the electron beam in the tube, the originally yellow  $WO_3$  was found to acquire a bluish cast indicating the formation of blue  $W_2O_5$ . Chemical decomposition was tested for by running, at very low power, critical points of emission lines from a fresh target in order to observe any changes in their position or width with time. As no changes were observed, it was concluded that either (1) the amount of chemical change was negligible, (2) it took place too quickly to be detected, or (3) the emission lines of  $WO_3$  and  $W_2O_5$  are similar. The second possibility is unlikely. If either the first or third is correct, the width and wave-length of the  $WO_3$  lines were obtained.

The wave-lengths of lines and edges were obtained by accurately locating their  $(l+l)$  positions and reading off their angles in four microscopes. The  $(l-l)$  angles were subsequently obtained and the computed diffraction angles corrected for the height of the slits and reduced<sup>8</sup> to a temperature of 18°C. Calibration corrections for the spectrometer circle, which are always less than 0.3'' of arc, were neglected.

#### Widths of absorption edges and emission lines

It has been shown by Richtmyer, Barnes and Ramberg<sup>9</sup> that the absorption coefficient of a metal as a function of the frequency in the neighborhood of an x-ray absorption edge is given by

$$\mu(\nu) = c \left\{ \frac{1}{2} - \frac{1}{\pi} \tan^{-1} \left( \frac{\nu_{E_0} - \nu}{\Gamma/2} \right) \right\}$$

if there is a uniform density of unoccupied states in the valence bands. Here  $\nu_{E_0}$  is the frequency corresponding to absorption into the first empty level above the Fermi surface and  $\Gamma$  is the full width at half maximum of the x-ray level involved in the absorption. The position of  $\nu_{E_0}$  on the absorption edge is characterized by an

<sup>8</sup> J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 19 (1935).

<sup>9</sup> Richtmyer, Barnes and Ramberg, Phys. Rev. **46**, 843 (1934).

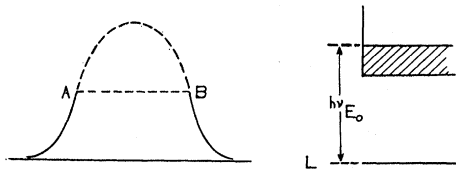


FIG. 1. (left) The shape of an emission band expected from considerations similar to those of Richtmyer, Barnes and Ramberg. *A* and *B* denote the inflection points on its sides. Their separation is the width of the region of occupied valence states. The sides below  $\overline{AB}$  are arc tangent curves.

FIG. 2. (right) Energy level diagram for x-ray absorption and emission transitions between an *L* level and a valence band.  $h\nu E_0$  denotes energy of transition to Fermi surface. Shading designates region of filled states.

inflection point. These authors have also shown that even if the distribution of states is not uniform, the absorption edge will still have very nearly the same arc tangent form on the low frequency side of  $\nu E_0$  and the position of  $\nu E_0$  will still be at the inflection point on the edge. From this equation, the widths of the *L* levels of tungsten and platinum were obtained by finding for each absorption edge the best match on the low frequency side of the inflection point in a set of arc tangent curves drawn with various values of the parameters *C* and *F*. The widths so obtained were corrected for the rocking curve width of the crystals according to the equation of Parratt.<sup>10</sup> This correction amounted to between 0.5 and 1.0 electron volt in the present measurements. These widths are listed in Table I. Also listed for comparison are the results obtained by Richtmyer, Barnes and Ramberg<sup>9</sup> for the widths of the *L* levels of gold. The present results are seen to be in good agreement with these. The value of  $3.6 \pm 0.5$  electron volts obtained for the *L*<sub>III</sub> level of platinum agrees within the experimental errors with the value  $4.1 \pm 0.5$  ev obtained by Beeman and Friedman.<sup>5</sup> From these widths, the widths of the other levels of tungsten and platinum could be obtained if the widths of their other emission lines were known, since it has been shown<sup>11</sup> that the width of an emission line is the sum of the widths of the initial and final states involved. In some preliminary tests, the width of the *L* $\beta_2$  line of tungsten involving the transition *L*<sub>III</sub>→*N*<sub>V</sub> was

found to be 10.6 electron volts. This gives a width of 7.2 electron volts for the *N*<sub>V</sub> level.

In the case of an emission line which arises from transitions from the filled states of a uniform density distribution of states in the valence bands to an unoccupied x-ray level, considerations similar to those of Richtmyer, Barnes and Ramberg<sup>9</sup> in the case of absorption limits show that its sides should have the shape of arc tangent curves below their inflection points. These two inflection points, designated by *A* and *B* in Fig. 1, mark the beginning and end of the transitions from the band of filled states. Their separation gives the width of the band. This is illustrated in Fig. 1 where *A* and *B* mark the inflection points on the sides of the emission band. (See footnote 6 in reference 7 for discussion of more general case.) This method of consideration is only valid if the width of the x-ray level is considerably less than the width of the band of filled valence states. The widths of the bands of filled valence states obtained in this manner are listed in Table II.

#### WAVE-LENGTHS OF ABSORPTION LIMITS AND EMISSION LINES

The theory of Richtmyer, Barnes and Ramberg mentioned above indicates that it is logical to call the inflection point in an absorption edge the position of the edge. This point corresponds to the transition from an x-ray level into the lowest unoccupied level in the valence band. This is the transition of energy  $h\nu(E_0)$  in the energy level diagram of Fig. 2. For every absorption edge, there should be an emission band corresponding to transitions from the filled portions of the valence band to the x-ray level. Its high frequency side should coincide in wave-length with that of the absorption edge because the region of filled states leaves off where the region of empty states begins. This is seen to be the case for the *L* edges of tungsten metal and its oxide in Figs. 3 to 8, where the edges and their corresponding emission lines

TABLE II. Widths of bands of filled valence states.

TRANSITION	LINE	WO <sub>3</sub>	W
	<i>L</i> $\gamma_4$	16.2 ev	16.2 ev
5 <i>d</i> , 6 <i>s</i> band→ <i>L</i> <sub>I</sub>	<i>L</i> $\gamma_4''$	$12.0 \pm 6.0$	$12.0 \pm 4.0$
5 <i>d</i> , 6 <i>s</i> band→ <i>L</i> <sub>II</sub>	<i>L</i> $\gamma_6$	$10.5 \pm 1.0$	$7.0 \pm 0.5$
5 <i>d</i> , 6 <i>s</i> band→ <i>L</i> <sub>III</sub>	<i>L</i> $\beta_5$	$8.9 \pm 1.0$	$6.5 \pm 0.5$

<sup>10</sup> L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

<sup>11</sup> V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930).

have been plotted together on the same wave-length scale. For convenience, the wave-length has been replaced by a scale of ev with the edge inflection point arbitrarily chosen as zero. It is to be noticed that the relative position of lines and edges in these figures is independent of the choice of the edge inflection point locations, and depends only on the accuracy of angular determinations by the instrument, which is better than  $\pm 0.3$  ev.

In Table III the wave-lengths of edges and those of line peaks are listed and compared with the results obtained by previous investigators.<sup>12-15</sup> Because this older work was done with low resolving power instruments, the wave-length of the center of an edge, rather than that of its inflection point, was given. This causes

considerable disagreement with the present results in the cases where the edges themselves show structure, as occurs in the  $L_I$  edges. In all other cases, the agreement is seen to be good.

#### DISCUSSION

The density of states of the  $5d$  and  $6s$  bands of tungsten has been calculated by Manning and Chodorow<sup>6</sup> using the cellular method of Wigner and Seitz<sup>16</sup> as modified by Slater.<sup>17</sup> In this method use is made of Bloch's theorem

$$\psi(\mathbf{r}) = u(\mathbf{r}) \exp [i(\mathbf{k} \cdot \mathbf{r})]$$

which says that any wave function  $\psi(\mathbf{r})$  in a crystal is equal to a plane wave  $\exp [i(\mathbf{k} \cdot \mathbf{r})]$  times a function  $u(\mathbf{r})$  which is periodic with the

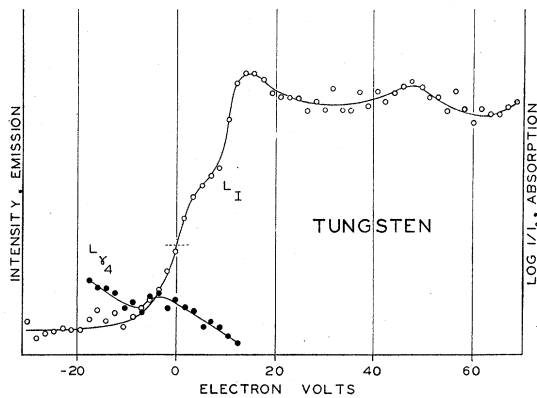


FIG. 3. The  $L\gamma_4'$ -emission line and  $L_I$ -absorption edge of tungsten.

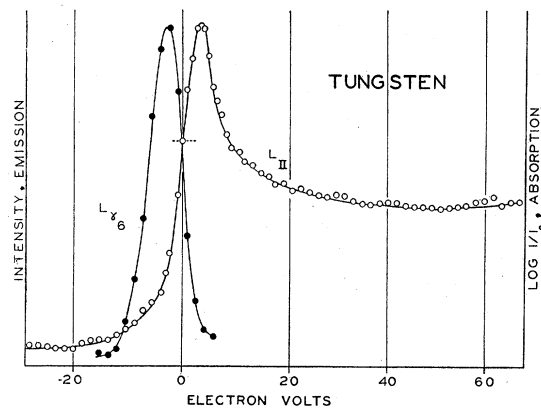


FIG. 5. The  $L\gamma_6$ -emission line and  $L_{II}$ -absorption edge of tungsten.

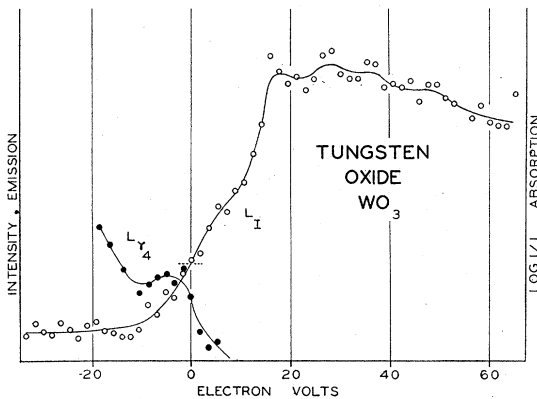


FIG. 4. The  $L\gamma_4'$ -emission line and  $L_I$ -absorption edge of tungsten oxide ( $WO_3$ ).

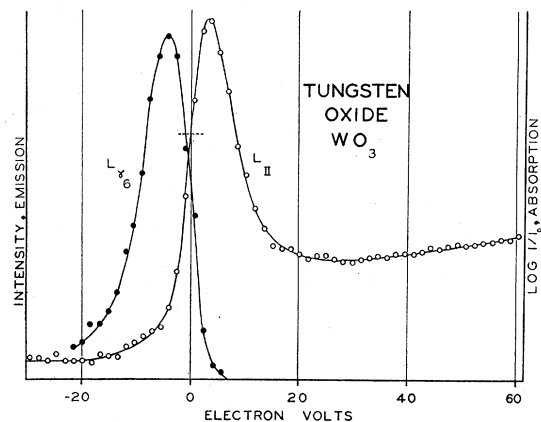


FIG. 6. The  $L\gamma_6$ -emission line and  $L_{II}$ -absorption edge of tungsten oxide ( $WO_3$ ).

<sup>12</sup> Y. Nishina, *Phil. Mag.* **49**, 521 (1925).

<sup>13</sup> E. Friman, *Zeits. f. Physik* **39**, 813 (1926).

<sup>14</sup> S. Idei, *Sci. Rep. Tohoku Imp. Univ.* **19**, 559 (1930).

<sup>15</sup> A. Sandström, *Zeits. f. Physik* **65**, 632 (1930).

<sup>16</sup> E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933).

<sup>17</sup> J. C. Slater, *Phys. Rev.* **45**, 794 (1934).

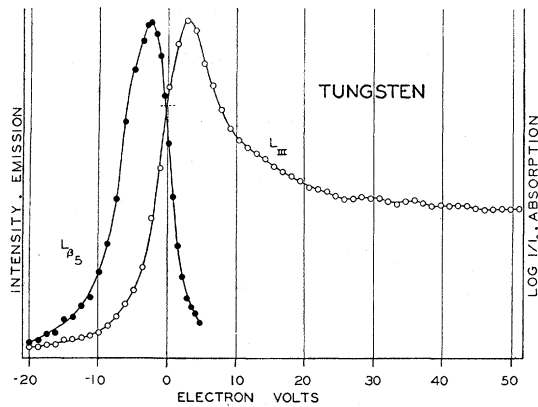


FIG. 7. The  $L\beta_5$ -emission line and  $L_{III}$ -absorption edge of tungsten.

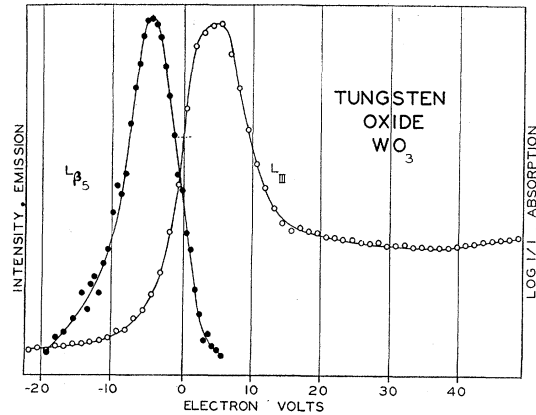


FIG. 8. The  $L\beta_5$ -emission line and  $L_{III}$ -absorption edge of tungsten oxide ( $WO_3$ ).

period of the lattice. The tungsten lattice is partitioned into fourteen-sided polyhedra by drawing planes perpendicular to radii between nearest and next nearest neighbors at the midpoints. Bloch's theorem shows that the behavior of  $\psi(\mathbf{r})$  in one polyhedral cell determines its behavior throughout the lattice. The Schrodinger equation must then be solved in one cell, subject to the condition of lattice periodicity of  $u(\mathbf{r})$ . A nearly self-consistent tungsten metallic field was used. Wave functions were taken to be linear combinations of fourteen independent wave functions whose angular parts were the fourteen lowest spherical harmonics. The coefficients in the combination were determined by satisfying the Bloch conditions at the midpoints of all cell faces. This was only carried out for certain directions of the wave vector  $\mathbf{k}$ . In this treatment several approximations were used, since in principle, the wave functions should contain *all* spherical harmonics and the Bloch conditions satisfied over the *whole* cell surface for *all* values of  $\mathbf{k}$ . Furthermore the cellular method makes no attempt to include interactions between specific pairs of particles. Manning and Chodorow have pointed out that exchange between valence electrons would have the effect of narrowing the  $5d$  and  $6s$  bands over the results actually obtained. However, from their calculated results, shown in Fig. 9, the electrical conductivity, electronic specific heat, and paramagnetic susceptibility were computed and all but the last were in good agreement with experiment. The fact that their magnetic

susceptibility was too small is probably due to the neglected tendency of electrons with parallel spins to keep apart.

The density of states  $n(E)$  enters into the intensity  $I(E)$  of an x-ray transition through the equation

$$I(E) = n(E)p(E),$$

where  $p(E)$ , the transition probability, is also a function of the energy. The transition probability  $p(E)$  may be taken as proportional to the amount of  $p$  function used in the metallic wave function of energy  $E$  in the case of transitions involving the  $L_I$  level since this is an  $s$  level and the  $l$  selection rule permits only  $s \rightarrow p$  transitions. Similarly  $p(E)$  in the case of  $L_{II}$  or  $L_{III}$  transitions may be taken proportional to the sum of the amounts of  $d$  and  $s$  function, as  $L_{II}$  and  $L_{III}$  are  $p$  levels. The overlapping of atomic  $5d$  wave functions in the tungsten lattice is small enough

TABLE III. Wave-lengths of edges and those of line peaks.

TUNGSTEN		PRESENT RESULTS	PREVIOUS RESULTS
$L_I$	W	1.02253A	1.0205 <sup>12</sup>
	$WO_3$	1.02219	
$L_{\gamma_4}$	W	1.02595	1.0258 <sup>13</sup>
	$WO_3$	1.02596	
$L_{II}$	W	1.07215	1.0713 <sup>12</sup>
	$WO_3$	1.07189	
$L_{\gamma_6}$	W	1.07232	1.0721 <sup>14</sup>
	$WO_3$	1.07233	
$L_{III}$	W	1.21252	1.2116 <sup>12</sup>
	$WO_3$	1.21220	
$L\beta_5$	W	1.21294	1.2129 <sup>14</sup>
	$WO_3$	1.21296	
Platinum			
$L_I$		0.89088	0.8914 <sup>15</sup>
$L_{II}$		0.93213	0.9321 <sup>15</sup>

so that the mixing of states in the  $5d$  band is not great, and is less for the low energy portions of the band than the high. This means that the  $5d$  band consists chiefly of  $d$  states and one would expect  $L_{II}$  and  $L_{III}$  x-ray spectra to reflect closely the shape of the density-of-states in the  $5d$  band. In the  $6s$  band which overlaps the  $5d$ , mixing is much greater; in the  $6p$  and higher bands it is probably very great indeed, the density of states from there on being dependent chiefly on the crystal structure.

The experimental absorption and emission spectra of tungsten are seen to be in good agreement with this picture of its band structure. The shape of the  $L_{II}$  and  $L_{III}$  edges is very similar to that of the calculated density-of-states. The high maximum of initial absorption is several volts broader than the corresponding maximum of empty states in the  $5d$  band, due to the width of the  $L$  levels. The lack of structure at higher frequencies may be due to the thorough mixing of the higher states plus the double  $p \rightarrow s$ ,  $p \rightarrow d$  possibility for transitions from the  $L_{II}$  and  $L_{III}$  levels. The  $L_I$  edge, on the other hand, shows only a small initial absorption due to the low density of  $p$  states in the  $5d$  and  $6s$  bands. This increases in a second jump upon reaching the  $6p$  band where there is an extra high density of  $p$  states which drops off at higher energies. The general increase in structure over that of the  $L_{II}$ ,  $L_{III}$  edges may be ascribed to the fact that absorption into only one type of state, a  $p$  state, is possible. The emission lines do not show the double peak exhibited by the calculated density of occupied  $5d$  states. Furthermore, their widths are considerably less, 6.5 and 7.0 eV compared to the calculated band width of 10 electron volts. It may be that the band is narrowed by exchange to such an extent that the two peaks are no longer resolvable because of the width ( $>3.0$  eV) of the  $L$  levels. The fact that the particular atom partaking in an x-ray transition is ionized in either the initial or final state may also tend to narrow the energy spread of states in its neighborhood. The low intensity of the  $L\gamma_4''$ -emission line compared to that of the  $L\gamma_6$  and  $L\beta_5$  lines is also due to the low  $p$  character of the  $5d$  and  $6s$  bands. The asymmetry of these lines is due to the sharp cut-off of filled states at the Fermi level.

A comparison of the corresponding edges and lines of metallic tungsten and tungsten oxide ( $WO_3$ ) shows that the oxide absorption edges are shifted about 2.5 volts to higher energy although the emission line peaks show no such shift. Both the emission lines and the high initial absorption maxima of the  $L_{II}$  and  $L_{III}$  edges are broadened by several volts, which is considerably more than any spurious broadening due to inhomogeneities in the absorbers. The

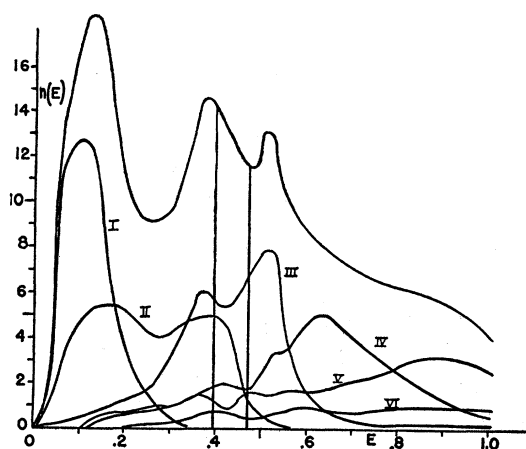


FIG. 9. Density of states in  $5d$  and  $6s$  bands of tungsten (reference 6). Energy is given in atomic units. Upper curve is total density of states. Curves I to VI give densities in component bands. Right-hand vertical line gives level to which states are filled in tungsten.

shift of the edges may be due to a weaker binding in the oxide; however, exact data are not available. The broadening of the absorption maximum is due to electrons leaving the  $5d$  band where they spend relatively little time near the oxygen atoms to go into the  $6s$  and  $6p$  bands where the time spent near oxygen atoms is considerably greater. This is possible because the high electronegativity of oxygen lowers the energy of the latter states over that of the former. These lower bands are broader than the  $5d$  and have a lower density of states. Hence the broadening of the emission lines.

There are available, at present, no calculations of the band structure of platinum; however, from its large electronic contribution to the specific heat, anomalous temperature coefficient of resistance at high temperatures, and large paramagnetism, one expects it to have a high but rapidly decreasing density of vacant  $5d$  states

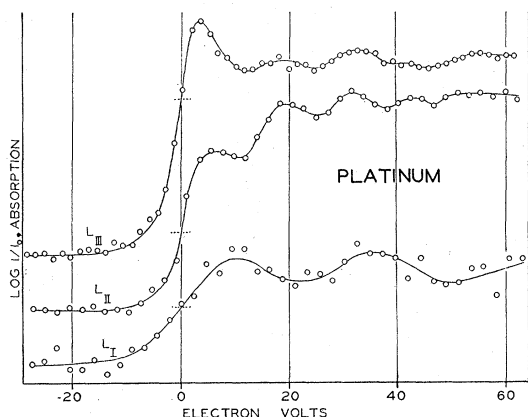


FIG. 10.  $L$ -absorption edges of platinum. Circles are experimental points. Positions of flex points are denoted by dashed lines. Edges are plotted to same energy scale and adjusted so that flex points coincide at point arbitrarily taken as the zero of the energy scale.

at the surface of the Fermi level. Because  $6s$  electrons overlap more than do  $5d$ , one expects the  $6s$  band to be broad, highly mixed, overlapping the  $5d$ . Due to the increase in nuclear charge in going from W to Pt, which contracts the electronic orbits, one expects all bands in Pt to be narrower and their states to show less mixing than in the corresponding bands of W.

Again, the  $L$  absorption edges, shown in Fig. 10, are in agreement with the band picture. The  $L_{II}$  and  $L_{III}$  edges show a high initial absorption, while that of the  $L_I$  edge is small. There is much more structure corresponding to less mixing of states, due chiefly to the forbidding of  $p \rightarrow p$  transitions in the  $L_{II}$  and  $L_{III}$  edges. It will be seen that although the positions of  $L_{II}$  and  $L_{III}$  structure features are in good agreement, their relative intensities are not. For example, the initial  $L_{III}$ -absorption peak is only a knee in the  $L_{II}$  edge. Differences in the  $L_{II}$  and  $L_{III}$  edges have also been recorded by other observers.<sup>18</sup> The  $L_{II}$  and  $L_{III}$  levels differ only in their  $j$  value. A large spin orbit coupling of the metallic valence electrons would suffice to account for these differences in a satisfactory manner.

It is a pleasure to acknowledge our indebtedness to Dr. Irving Langmuir of the General Electric Company for preparing the very pure tungsten foils and oxide used in this work. We are also grateful to the American Philosophical Society for a grant-in-aid, and to members of the Baltimore-Washington Solid State Seminar for valuable suggestions and discussions.

<sup>18</sup> J. Veldkamp, *Physica* 2, 25 (1935).

## Fluorescent $K$ X-Rays from Ions in Solution and from Gases

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The  $K\alpha$  lines emitted by cobalt, nickel, copper and bromine contained in chemical compounds were compared with the lines emitted by these elements in pure form. Chemical combination was found to broaden the lines and increase their asymmetry. The magnitude of the effect was greatest for cobalt, progressively smaller for nickel and copper and completely unobservable in the case of bromine. The further effect on the  $K\alpha_1$  lines of putting these compounds into water solution at various concentrations was studied. It was found that the lines were unchanged by solution regardless of the dilution. Finally, the  $K\alpha$  doublets of liquid and gaseous bromine were studied and found to be identical, showing that the state of physical aggregation has no effect on the  $K\alpha$  lines of this element.

### INTRODUCTION

THE chemical state of an element is known to affect the shape, width, wave-length and relative intensity of its x-ray emission lines.

Because the forces involved in chemical and physical binding are in no way greatly different, the physical state of an element is expected to affect its emission lines just as its chemical state