

<sup>17</sup> The calculations also indicate the approximate equivalence in energy (and abundance) of  $^1\Pi$  and  $^3\Pi$  states. Thus, crudely the ratio of  $\delta g$  to the electronic rotational moment  $g_r^e$  ought to be  $A^2/B(E_{i_0} - E_i)$ , where the energy difference is an average energy difference for the  $^1\Pi$  and  $^3\Pi$  states. Using the same value for the parameters as in the estimation of  $\delta g$ ,  $g_r$  would be expected to be about a factor of ten smaller than  $\delta g$ .

<sup>18</sup> A. Carrington, G. N. Currie, D. H. Levy, and T. A. Miller, *J. Chem. Phys.* **50**, 2726 (1969).

<sup>19</sup> A. Carrington, P. N. Dyer, and D. H. Levy, *J. Chem. Phys.* **47**, 1756 (1967).

<sup>20</sup> H. E. Radford, *J. Chem. Phys.* **40**, 2732 (1964).

<sup>21</sup> Recent measurements on  $^2\Pi$  SeH (Ref. 10) require some qualification in this statement. Apparently, measurements in a single additional level—assuming less than infinite accuracy—will not determine  $\delta g$  and  $A$  uniquely if there is resolved  $\Lambda$  doubling as is the case with the SeH and TeH molecules.

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## Photoionization of Europium and Thulium: Threshold to 1350 Å\*

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Photoionization spectra of europium and thulium are reported from threshold to 1350 Å. The ionization efficiency in this region is found to be dominated by autoionization. Autoionization structure, believed to be due to  $4f^N 6s^2 \rightarrow 4f^{N-1} 5dnp$  transitions, is interpreted and other strong resonances listed. The ionization potential of europium is determined to be  $5.664 \pm 0.008$  eV and that of thulium to be  $6.180 \pm 0.008$  eV.

### INTRODUCTION

The emission spectra of the lanthanide elements tend to be extremely complex due to core  $4f$  electron excitation and the occurrence of multiple electron excitations of the outer  $6s^2$  electrons. Due to the complexity of the large numbers of lines, the ionization potentials of most of the lanthanides are either not known spectroscopically or are determined from Rydberg series in each of which only a few members are known. A determination of the ionization potential to good accuracy would be of aid in interpreting these complex emission spectra. The ionization potential is also important in the determination of the bond energies of the lanthanide metallic oxides and sulphides and other diatomics by dissociative ionization. The photodissociative ionization technique, combined with accurate ionization potentials, would give the bond energies for these molecules a factor of ten more accurate than the current thermochemical values. In addition to the ionization potential, the photoionization technique yields information about position and relative intensity of highly excited states of the neutral atoms which autoionize.

Barium, which is just previous in the periodic table to the start of the lanthanide series, exhibits strong autoionization.<sup>1</sup> Ytterbium, which has  $4f^{14}6s^2$  outer electrons, is dominated completely by autoionization.<sup>2</sup> In both barium and ytterbium the dominant excitation is the  $(\text{core}) + 6s^2 \rightarrow \text{core} + 5dnp$  which for appropriate  $n$  values lie above the ionization limit. Other excitations such as the  $4f^{14}6s^2 \rightarrow 4f^{13}6s5dnd$ ,  $4f^{14}6s^2 \rightarrow 4f^{13}6s^2nd$ , and  $4f^{14}6s^2 \rightarrow 4f^{14}6pnd$  appear to have been observed in ytterbium but are less well substantiated. It is likely then that these transitions could also give important resonances in europium and thulium. As will be seen, autoionization due to excitation of both

$6s^2$  electrons or an excitation of a core  $4f$  electron is important in photoabsorption and ionization of europium and thulium.

This work describes and gives a partial analysis of the photoionization spectra of europium and thulium from threshold to 1350 Å. Europium has been studied extensively by Russell and King<sup>3</sup> who classified many of the configurations arising from the excited states of the atom, including some of those from the two electron series such as  $4f^7(5d6p)$ . They also determined the ionization potential of europium from several Rydberg series of few members each to be  $5.67 \pm 0.01$  eV. Smith and Wybourne<sup>4</sup> analyzed the spectrum and reassigned some of the levels in the excited configurations. Smith and Collins<sup>5</sup> identified an upper  $^8P$  term from the  $5d6p$  configuration which was incorrectly identified by Russell and King and did not fit into Smith and Wybourne's calculations.

The principal studies of thulium were performed by King<sup>6</sup> and Meggers.<sup>7,8</sup> King classified 250 lines as a function of temperature and Meggers classified the ground state as being  $4f^{13}6s^2\ ^2F_{7/2}$ . Camus and Blaise<sup>9</sup> identified a number of configurations and the terms arising from them. Their most recent determination of the ionization potential of thulium is  $6.22 \pm 0.02$  eV.<sup>10</sup>

Reader and Sugar<sup>11</sup> have calculated the ionization potentials of the lanthanides and give values of 5.68 and 6.18 eV for europium and thulium, respectively. Hertel<sup>12</sup> measured the ionization potentials of europium and thulium by the surface ionization technique and obtained  $5.64 \pm 0.05$  eV for europium and  $6.03 \pm 0.04$  eV for thulium. Zmbov and Margrave<sup>13</sup> using electron impact techniques measured the ionization potentials of europium to be  $5.61 \pm 0.10$  eV and thulium to be  $5.87 \pm 0.10$  eV. The electron impact data suffers from ambiguity of determining a threshold when

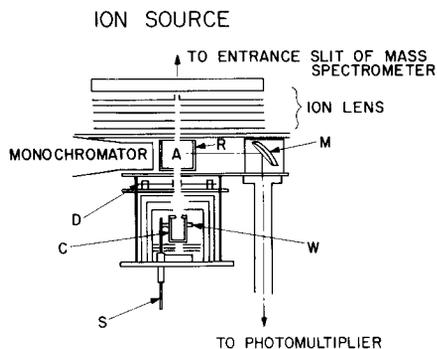


FIG. 1. Diagram of the high temperature source of the mass spectrometer. A, ionization region; R, repeller electrode; M, mirror to reflect light to photomultiplier; D, thermal ion deflectors; C, crucible; W, tungsten heating filament; S, support rods for tungsten filament.

autoionization is present, as the present results show, and it is therefore expected that these values could differ from the more accurate photoionization and spectroscopic results. A more complete review of the data available on the lanthanide optical excitations and ionization limits is contained in the *Bibliography on the Analysis of Optical Spectra*.<sup>14</sup>

#### EXPERIMENTAL TECHNIQUE

The photoionization mass spectrometer used was essentially the same as reported earlier.<sup>15,16</sup> A dc discharge in hydrogen was used to excite the hydrogen continuum<sup>17,18</sup> which furnishes light from the visible blue to 1600 Å. Below 1600 Å the hydrogen many-line spectrum was generated under the same operating conditions as the hydrogen continuum. The pressure in the discharge tube was maintained at 10 mm Hg and a current of 1.5–2.0 A at about 700 V was passed through the discharge tube. The dc current supply<sup>19</sup> maintained a constant current to better than 1% which provided for stability of the light intensity. An estimated light flux is  $10^{10}$  photons/sec·Å for the continuum radiation at 2200 Å. The bandpass of the monochromator was 3 Å for these experiments.

Figure 1 shows a cross section of the source of the mass spectrometer used in these experiments. A beam of atoms effuses from the crucible C. The crucible is heated by a tungsten filament W, supported by tungsten rods S. Thermal ions produced by the crucible are deflected by the electrostatic deflectors D. The neutral beam then intersects the photon beam in the region labelled A. The ions created in this region are repelled toward the ion lens and mass analyzer by repeller electrodes R. The ions are then counted or measured dc with an electron multiplier. The statistical error in this measurement is 5%–8%. The light which has passed through the ionization region is reflected by a MgF<sub>2</sub>-coated aluminized concave mirror to the photomultiplier. The reflectivity of the mirror was checked and found to be independent of wavelength down to 1350 Å. The photomultiplier was an EMI 9524S<sup>20</sup> coated with sodium salicylate. The sodium salicylate

was assumed to have a flat response from 2200 Å to 1350 Å.<sup>21</sup>

The temperature of the crucible was controlled by regulating the current through the filament W. The temperature scale was calibrated in a separate experiment outside the mass spectrometer with an optical pyrometer. The temperature was found to remain constant when a constant current was maintained in the heater filament. The absolute temperature scale was not important in these experiments as all that was required was a constant intensity atomic beam.

Thermal excitation of the neutral beams of thulium and europium was not present to any measurable degree. The nearest excited state in europium is the  $4f^7 6s^2 d^1 a^{10} D_{5/2}$  which lies 13 000 cm<sup>-1</sup> above the  $4f^7 6s^2$  <sup>8</sup>S ground state. The  $4f^{13} 6s^2$  <sup>2</sup>F<sub>7/2</sub> ground state of thulium is separated by 8771 cm<sup>-1</sup> from the  $4f^{13} 6s^2$  <sup>2</sup>F<sub>5/2</sub> first excited state. The temperature of the crucible in these experiments was about 1000°K and assuming Boltzmann statistics the thermal excitation would be less than 10<sup>-5</sup>.

The thulium and europium were purchased from ESPI<sup>22</sup> and stated to have a purity of 99.9%.

#### RESULTS AND INTERPRETATION

##### Europium

Figure 2 gives the photoionization spectrum for europium from threshold to 1350 Å. The curve represents the ion intensity divided by photon intensity and hence is proportional to the photoionization cross section. From threshold at 2189 Å ( $E = 45\,680$  cm<sup>-1</sup>) to 1750 Å, the spectrum is dominated by autoionization as indicated by the strong resonance lines. From 1750 to 1350 Å the curve is essentially smooth and gradually decreasing in amplitude. At wavelengths longer than 2189 Å there is no detectable ionization and the rapidity of the onset of 2189 Å establishes an upper limit for the ionization potential. The inset in Fig. 2 shows the threshold region on an expanded wavelength scale.

Even though the threshold is somewhat obscured by the autoionization there is strong reason to interpret it as the ionization potential. First of all, autoionization will only occur when the excited state lies above the ionization potential and due to the large number of expected transitions in this region, such as the  $5d^7 p(^3P)^8 P_{3/2}$  at about 2200 Å, the ionization potential must be between 2200 and 2189 Å. Second, there is an underlying background of ionization efficiency which is suggestive of the direct ionization process which has as its threshold the ionization potential. The direct process may be perturbed by a resonance line and could be decreased in amplitude near a resonance but should be detectable away from a resonance line. Third, a detailed study of the first resonance line, which is broader than the bandpass of the monochromator, indicates that the leading edge rises abruptly within the bandpass of the monochromator exactly as in a

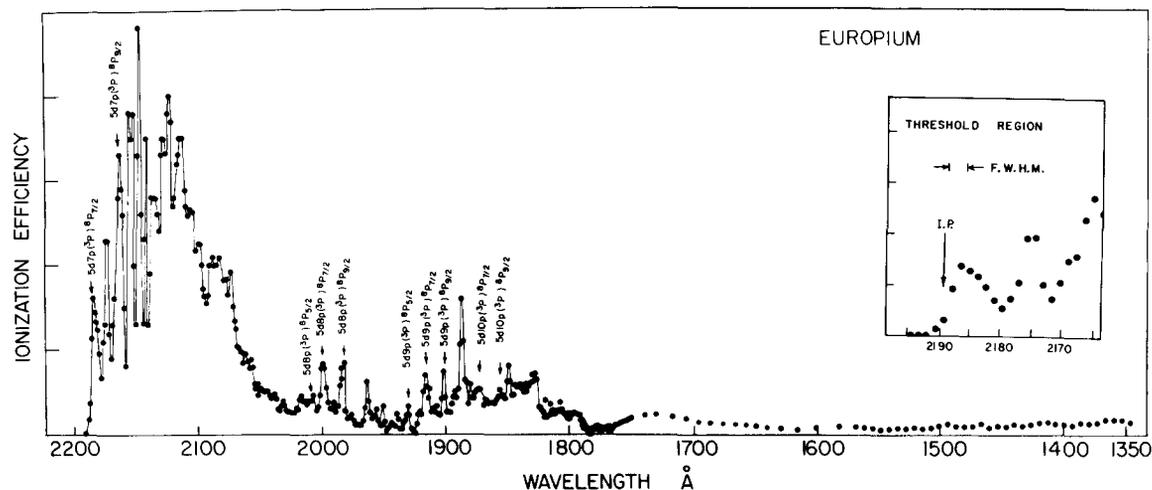


FIG. 2. Photoionization efficiency curve for europium. The horizontal axis is wavelength in angstroms and the vertical axis is ionization efficiency. Ionization efficiency is ion intensity divided by photon intensity. The insert shows the threshold region on an expanded wavelength scale. The ionization potential (I.P.) is shown and the full width at half-maximum (fwhm) of the monochromator is indicated. The fwhm is taken to be the error in determination of the I.P.

normal threshold. It is felt that even though at first inspection the threshold may seem obscure the reasons given above are strong evidence for interpreting the ionization potential at 2189 Å, i.e., the point at maximum slope on the leading edge.

The ground state of Eu is  $4f^7 6s^2 \ ^8S_{7/2}$ . Under the selection rule  $\Delta J = 0, \pm 1$  the only optically accessible states are those with  $J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ . If the coupling is essentially Russell-Saunders for a given configuration, then the selection rules  $\Delta S = 0$  and  $\Delta L = 0, \pm 1$  would be obeyed. However, if the coupling undergoes a change in character with increasing excitation, departures from these rules might be expected. Intercombinations as well as violations of  $\Delta L = 0, \pm 1$  may occur with appreciable probability as is observed in Yb.<sup>2</sup> The normal channel for ionization would be  $4f^7 6s^2 \ ^8S_{7/2} \rightarrow 4f^7 6s \ ^8P$ . In the case of Eu as in Ba and Yb the threshold for this process is competing with autoionization processes which satisfy the selection rule  $\Delta J = 0, \pm 1$ . Among the possible transitions are  $4f^7 6s^2 \rightarrow 4f^7 5dnp$  and  $4f^7 6s^2 \rightarrow 4f^6 5d^2 6s$  where one electron has a  $\Delta l = \pm 1$  and the other  $\Delta l = 2$ . The  $5dnp$  excitations are particularly strong in Ba and Yb and hence might be expected to be prominent in Eu.

The  $5d6p$  configuration of Eu has two  $^8P$  states. The lower of these was designated  $x^8P$  by Russell and King and a higher one designated  $v^8P$  by Russell and King but with incorrect assignment as to energies.<sup>5</sup> Smith and Collins have reassigned the energies of the upper  $^8P$  state in a manner consistent with their calculation, and have suggested the states be called  $5d6p(^3P_1)^8P$  for the lower  $^8P$  and  $5d6p(^1P_1)^8P$  for the higher  $^8P$  levels. The  $5d6p(^3P_1)^8P$  levels have as their series limit the  $5d^9D$  levels of Eu II while the  $5d6p(^1P_1)^8P$  levels have as their limit the  $5d^7D$  levels of Eu II.

As the coupling of the two excited electrons under-

goes changes with increasing excitation, the description of the configurations change. For descriptive purposes to associate those levels which form a series, we will simply give an  $L$  value and an  $S$  value for the excited electrons. For example, then the next member of the series after the  $5d6p(^3P_1)^8P$  would be called  $5d7p(^3P)^8P$ .

The  $5d7p(^1P)^8P$  levels are expected to lie at about  $52\,000\text{ cm}^{-1}$  and the  $5d8p(^1P)^8P$  at about  $57\,000\text{ cm}^{-1}$ . There is no structure at  $57\,000\text{ cm}^{-1}$  that could be assigned to this series. The  $5d7p(^1P)^8P$  levels would then lie in the same region as the  $5d9p(^3P)^8P$  levels which makes interpretation difficult.

The first strong line lying right at threshold is identified as the  $4f^7 5d7p(^3P)^8P_{7/2}$ . The first member of this series, the  $4f^7 5d6p(^3P)^8P_{7/2}$  was identified by Russell and King as having an energy of  $34\,726\text{ cm}^{-1}$  with a Rydberg denominator of 2.23. The  $5dnp(^3P)^8P_{7/2}$  series has as its limit the  $5d^9D_5$  level of Eu II which lies at  $10\,643\text{ cm}^{-1}$  above the ground state of Eu II. This energy must be added to the ionization potential of Eu I to obtain the series limit. The levels that seem to fit into the  $5dnp(^3P)^8P$  series by the Rydberg denominator scheme are tabulated in Table I.

The third strong resonance line at  $2166\text{ Å}$  is interpreted as the  $4f^7 5d7p(^3P)^8P_{9/2}$  level. The first member of this series was identified by Russell and King as lying at  $34\,726\text{ cm}^{-1}$  with a Rydberg denominator of 2.23. The lines which seem to fit the series going to  $5d^9D_6$  level of Eu II as a limit are tabulated in Table I.

The remaining member of the multiplet is the  $5dnp(^3P)^8P_{5/2}$ . The  $4f^7 5d6p(^3P_1)^8P_{5/2}$  was identified by Russell and King as being at  $33\,786\text{ cm}^{-1}$  with a Rydberg denominator of 2.23. The limit for this series would be the  $5d^9D_4$  state of Eu II which gives an energy limit for the series as  $55\,990\text{ cm}^{-1}$ . The  $5d7p(^3P)^8P_{5/2}$  would then be expected to lie at  $45\,470\text{ cm}^{-1}$  which is

TABLE I. Rydberg series of europium.

$E(\text{cm}^{-1})$	Identification	Rydberg Denominator
<i>5dnp</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub> limit <sup>9</sup> <i>D</i> <sub>6</sub> $E=56\ 810$		
34 726 <sup>a</sup>	<i>5d6p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub>	2.23
46 160	<i>5d7p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub>	3.22
50 435	<i>5d8p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub>	4.15
52 572	<i>5d9p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub>	5.10
53 887	<i>5d10p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>3/2</sub>	6.15
<i>5dnp</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub> limit <sup>9</sup> <i>D</i> <sub>6</sub> $E=56\ 320$		
34 102 <sup>a</sup>	<i>5d6p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub>	2.23
45 757	<i>5d7p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub>	3.23
50 040	<i>5d8p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub>	4.19
52 185	<i>5d9p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub>	5.17
53 355	<i>5d10p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>7/2</sub>	6.10
<i>5dnp</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>5/2</sub> limit <sup>9</sup> <i>D</i> <sub>4</sub> $E=55\ 990$		
33 786 <sup>a</sup>	<i>5d6p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>5/2</sub>	2.22
(45 470)	<i>5d7p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>5/2</sub>	(3.22) Unobserved
49 860	<i>5d8p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>5/2</sub>	4.23
51 806	<i>5d9p</i> ( <sup>3</sup> <i>P</i> ) <sup>8</sup> <i>P</i> <sub>5/2</sub>	5.21

<sup>a</sup> Levels reported by Russell and King.

about 10 Å below the threshold observed. Two lines observed which do fit the *5d8p* and *5d9p* members of this series are tabulated in Table I.

The remaining strong lines between threshold and 2050 Å are due to some other configurations or other members of the *5d7p* configuration. The only even configuration which can lead to autoionization are *4f<sup>6</sup>nd6s<sup>2</sup>*, *4f<sup>6</sup>5dmd6s*, and *4f<sup>6</sup>6p7s*. The *4f<sup>6</sup>nd6s<sup>2</sup>* series would have as their limit the *4f<sup>6</sup>6s<sup>2</sup>* configuration of Eu II. The *4f<sup>6</sup>5d6s<sup>2</sup>* ought to be around  $25\ 000 \pm 5\ 000\ \text{cm}^{-1}$ .<sup>23</sup> This would put the *4f<sup>6</sup>6d6s<sup>2</sup>* much too high, i.e., ca.  $E=60\ 000\ \text{cm}^{-1}$ , to account for the strong resonances at threshold. The *4f<sup>6</sup>6pnd* series would have as its limit the *4f<sup>7</sup>6p* level of Eu II. These levels start at about  $23\ 500\ \text{cm}^{-1}$ , giving a series limit of  $\sim 70\ 000\ \text{cm}^{-1}$ . This would put the *6p6d<sup>3</sup>P* from this series at about  $56\ 000\ \text{cm}^{-1}$ , which is too high for resonance structure at threshold. The *4f<sup>7</sup>6p6s* levels are at ca.  $E=15\ 000\ \text{cm}^{-1}$ . This would put the *4f<sup>7</sup>6p7s* at about  $52\ 000\ \text{cm}^{-1}$  which cannot account for the structure at threshold. The only remaining choice is the *4f<sup>6</sup>5d<sup>2</sup>6s* term. It would seem then that the remaining unidentified strong resonances near threshold must belong to this configuration. The series arising from this configuration has as its limit the *4f<sup>6</sup>5d6s* of Eu II which starts at  $30\ 189\ \text{cm}^{-1}$  in Eu II.<sup>24</sup> Identification of these levels in this work is not possible as the remaining members of the series are not observed, e.g., the *4f<sup>6</sup>5d6s6d* ought to lie at  $65\ 000\ \text{cm}^{-1}$ . This region of the photoionization spectrum does not exhibit any strong resonance structure and hence identification of these series is not possible.

All the observed lines from europium photoionization are listed in Table II. The intensities are on an arbitrary scale. Energies were determined by the position of the maximum amplitude of the line.

## Thulium

Figure 3 gives the photoionization spectrum of thulium from threshold at 2006–1350 Å. The spectrum is dominated by autoionization from threshold to 1550 Å. From 1550 to 1350 Å the ionization efficiency is essentially constant with evidence of some autoionization of a low intensity. The inset of Fig. 3 is the threshold region on an expanded wavelength scale. The threshold is interpreted in the same manner as for europium. The ionization limit falls within the resonance line giving a rapid rise in ion intensity from zero.

One of the configurations which could be expected to give rise to autoionization near threshold in *Tm* is the *4f<sup>13</sup>5d6p*. The upper levels of this configuration ought to be near the ionization potential.<sup>25</sup> The limits for the series *4f<sup>13</sup>5dnp* would be the *4f<sup>13</sup>5d* levels of Tm II. Blaise and Camus<sup>9</sup> have identified 11 levels of this configuration and determined the *j* values of the levels. They did not, however, place any designations on the levels observed. The excited states of Tm I and Tm II are best described in terms of  $J_I(L_{II}S_{II})J_{II}$  coupling where the outer electrons are coupled according to *L-S* coupling with the resultant  $J_{II}$  and  $J_I$  of the core *JJ* coupled to provide a complete description of the state. By adding a <sup>2</sup>*D* electron to the core to form Tm II *4f<sup>13</sup>(7/2)5d* states, we would expect by our coupling scheme to get two sets of levels,

$$\left(\frac{7}{2}, \frac{3}{2}\right)_{5,4,3,2}$$

$$\left(\frac{7}{2}, \frac{5}{2}\right)_{6,5,4,3,2,1}$$

with the  $(\frac{7}{2}, \frac{5}{2})$  states center of gravity higher than the  $(\frac{7}{2}, \frac{3}{2})$  center of gravity. Bryant<sup>26</sup> reported the *4f<sup>13</sup>5d* scheme of Yb III in the  $J_I(L_{II}, S_{II})J_{II}$  scheme and comparison with the lowest ten levels of Tm II *4f<sup>13</sup>5d* suggests the scheme shown in Fig. 4.

Since the *LS* coupling selection rules approximately hold for the *LS* coupling outer electrons we expect the

TABLE II. Autoionizing lines of europium.

Intensity	Energy (cm <sup>-1</sup> )	Intensity	Energy (cm <sup>-1</sup> )
8	45 757	2.4	49 860
11.5	45 975	4	50 040
16.5	46 160	3.2	50 435
19	46 346	3	50 935
19	46 394	1.5	51 137
23	46 539	1.7	51 274
17.5	46 684	1.2	51 556
14	46 781	1.7	51 806
17.5	46 983	3.5	52 185
20	47 088	3.5	52 572
17.5	47 289	8	53 000
13.2	47 483	2.5	53 355
10.0	48 241	2.5	53 887
9.5	48 241	4	54 073
4.8	48 490		

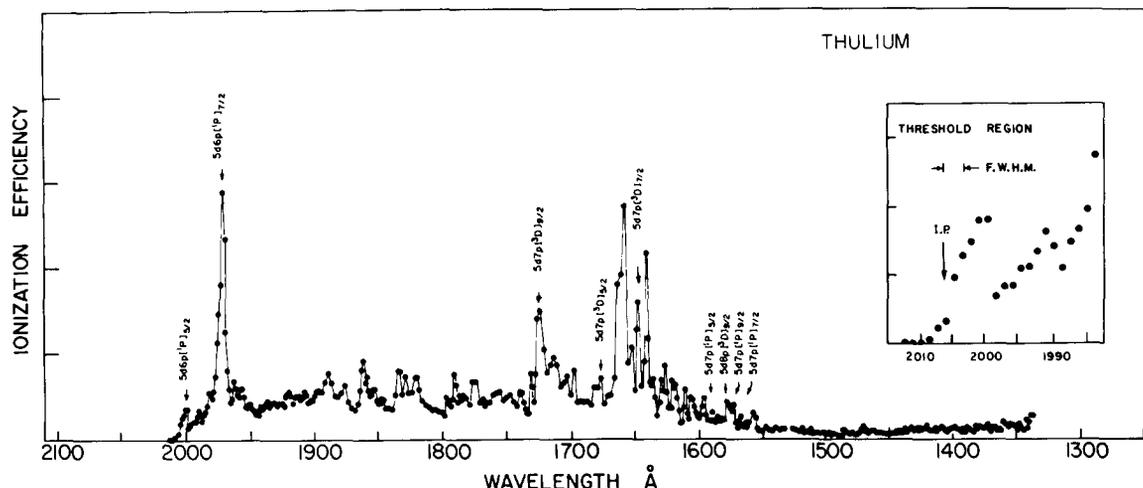
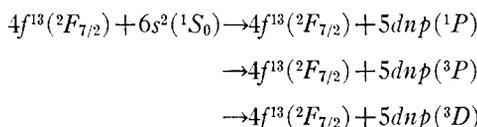


FIG. 3. Photoionization efficiency curve for thulium. The horizontal axis is wavelength in angstroms and the vertical axis is ionization efficiency. Ionization efficiency is ion intensity divided by photon intensity. The insert shows the threshold region on an expanded wavelength scale. The ionization potential (I.P.) is shown and the full width at half-maximum (fwhm) of the monochromator is indicated. The fwhm is taken to be the error in determination of the I.P.

strongest excitations to be

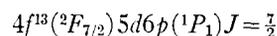


with total  $J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ .

In thulium as in europium the excited electrons undergo changes in coupling with increasing excitation. The best characterization of the states will then change. To identify the various series in thulium we will give an  $L$  and  $S$  value for the excited electrons and a total  $J$  for the state. For the following discussion of the  $4f^{13}(^2F_{7/2})5d6p$  configuration the  $J_1(L_{II}S_{II})J_{II}$  description will be used as some estimates of energies are available utilizing this description.<sup>25</sup>

The  $4f^{13}(^2F_{7/2})5d6p(^1P_1)J = \frac{7}{2}$  is expected to be the highest level of this group of levels. The  $J = \frac{5}{2}$  level is expected to lie about  $500 \text{ cm}^{-1}$  below the  $J = \frac{7}{2}$  level and the  $J = \frac{9}{2}$  level is expected to be about  $1500 \text{ cm}^{-1}$  below the  $J = \frac{7}{2}$  level.<sup>25</sup> If the strong reso-

nance at  $1972 \text{ \AA}$  is interpreted as the



level, the center of gravity of the  $^1P_1$  level is at  $\approx 50\,200 \text{ cm}^{-1}$ . Assuming that the  $^1P_1$  is the upper level and that it has as its limit, the  $(\frac{7}{2}, \frac{5}{2})$  levels, which have a center of gravity of  $\approx 73\,200 \text{ cm}^{-1}$ , one gets an approximate Rydberg denominator of 2.18 for the  $5d6p^1P_1$  levels.

The  $4f^{13}(^2F_{7/2})5d6p(^1P_1)J = \frac{5}{2}$  level would be expected to be  $500 \text{ cm}^{-1}$  below the  $J = \frac{7}{2}$  level and the line at  $1990 \text{ \AA}$  ( $E = 50\,241 \text{ cm}^{-1}$ ) is identified as such. The  $4f^{13}(^2F_{3/2})5d6p(^1P_1)J = \frac{9}{2}$  level lies below the ionization potential and is not observed. However, a line that seems to correspond to the  $4f^{13}(^2F_{7/2})5d7p(^1P)$ ,  $J = \frac{9}{2}$  is observed. A series of levels that seem to fit the general

TABLE III.  $^1P$  Rydberg series of thulium.

$E(\text{cm}^{-1})$	Identification	Rydberg denominator
$5dn p[^1P]_{7/2}$ limit $J = 3$ $E = 75\,136$		
50 709	$5d6p[^1P]_{7/2}$	2.12
63 857	$5d7p[^1P]_{7/2}$	3.11
$5dn p[^1P]_{5/2}$ limit $J = 4$ $E = 75\,119$		
50 241	$5d6p[^1P]_{5/2}$	2.14
62 920	$5d7p[^1P]_{5/2}$	3.15
$5dn p[^1P]_{3/2}$ limit $J = 5$ $E = 74\,755$		
63 613	$5d7p[^1P]_{3/2}$	3.14

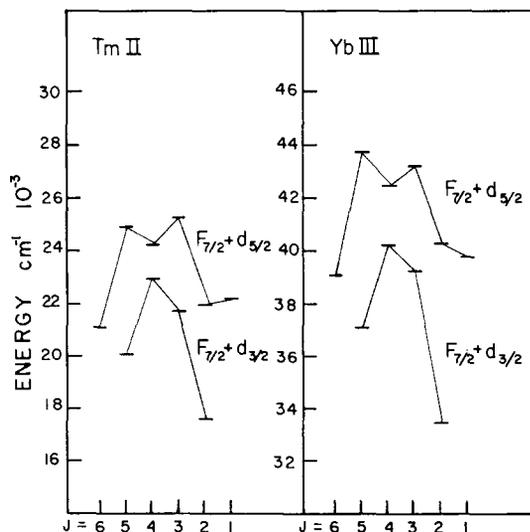


FIG. 4. The energies of the  $4f^{13}(^2F_{7/2})5d$  levels of Tm II and Yb III are plotted against  $J$  values for comparison.

TABLE IV.  $^3D$  Rydberg series of thulium.

$E(\text{cm}^{-1})$	Identification	Rydberg denominator
$5dn\phi[{}^3D]_{9/2}$ limit $J=5$ $F=70$ 074		
57 971	$5d7p[{}^3D]_{9/2}$	3.01
63 395	$5d8p[{}^3D]_{9/2}$	3.99
$5dn\phi[{}^3D]_{7/2}$ limit $J=4$ $F=72$ 754		
60 716	$5d7p[{}^3D]_{7/2}$	3.03
65 990	$5d8p[{}^3D]_{7/2}$	4.03
$5dn\phi[{}^3D]_{5/2}$ limit $J=3$ $E=71$ 559		
59 605	$5d7p[{}^3D]_{5/2}$	3.04

scheme is shown in Table III. The higher members of these series are not observed due to intensity variations in the series indicating the higher members of these series are not strongly mixing with those "allowed" transitions which make the multiple-electron transitions possible. Sugar<sup>25</sup> indicated the  $3D_1$  ought to lie  $5700\text{ cm}^{-1}$  below the  ${}^1P_1$  and the  ${}^3P_1$  ought to lie  $2800\text{ cm}^{-1}$  below the  ${}^1P_1$ . The  ${}^3D_1$ ,  ${}^3P_1$   $5d6p$  levels lie below the ionization potential and are not observed here. By using the approximate position indicated here and taking the limit of the  ${}^3D_1$ ,  ${}^3P_1$  levels as the  $(\frac{7}{2}, \frac{3}{2})$  levels we get Rydberg denominators of  $n^* \cong 2.00$  for the  $5d6p^3D_1$ , and  $n^* \cong 2.12$  for the  $5d6p^3P_1$ .

A series of levels which seem to correspond roughly to the  ${}^3D$  levels are shown in Table IV. The  $5d7p^3P$  levels ought to fall at about  $1650\text{ \AA}$ . The strong lines at  $1658\text{ \AA}$  are probably due to the  $5d7p^3P$  levels but lack of other levels and uncertainty about the expected splitting of the  ${}^3P$  levels make identification uncertain. It is noted that the  $4f^{13}(\frac{7}{2})5d6p^3P_1$ ,  $J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}$  levels in Yb II are split considerably with the  $J = \frac{7}{2}$  level lying

TABLE V. Autoionizing lines of thulium.

Intensity	Energy ( $\text{cm}^{-1}$ )	Intensity	Energy ( $\text{cm}^{-1}$ )
1.8	49 975	2.5	57 241
1.7	50 251	2.7	57 504
14.5	50 709	3.8	57 736
3.4	50 942	7.6	57 971
3.0	51 125	4.7	58 377
3.8	52 083	3.6	58 720
2.6	52 274	4.0	58 928
2.8	52 411	3.5	59 666
3.9	52 938	$\sim 10$	60 168
3.1	53 022	13.5	60 314
4.5	53 706	5.3	60 496
3.0	53 996	8	60 716
2.5	54 142	10.9	60 938
4.1	54 526	4.2	61 501
3.7	54 675	3.4	61 690
3.6	54 914	2.9	62 112
2.5	55 648	2.4	62 266
3.8	55 835	2.4	62 657
3.6	56 338	2.1	63 411
2.8	56 948	1.5	64 185

$\approx 8000\text{ cm}^{-1}$  below the  $J = \frac{9}{2}, \frac{5}{2}$ , levels.<sup>27</sup> If an approximately similar situation is observed in Tm for the  ${}^3P_1$  levels the  $\frac{7}{2}$  level would be lower than the  $\frac{9}{2}, \frac{5}{2}$  levels and probably is one of the strong lines between  $1750$  and  $1675\text{ \AA}$ .

The classification suggested here is only tentative and based primarily upon Rydberg denominator behavior and comparison with related spectra when possible. If the coupling and perturbations are undergoing change as a series progresses then the identification suggested here may be in error. Complete and unambiguous classification of the resonance lines observed must await more experimental results as well as detailed calculations of the energies of the various configurations.

Another probable configuration that would contribute to autoionization in the region observed would be the  $4f^{13}6s^2 \rightarrow 4f^{12}6s^2nd$  transitions. This configuration would have as its limits the  $4f^{12}6s^2$  levels of Tm II. The terms arising from this configuration in Tm II are  ${}^1SDGI$  and  ${}^3PFH$  of which only the  ${}^3H_6$ ,  ${}^3H_5$ , and  ${}^3F_4$  have been identified.<sup>28</sup> Camus<sup>29</sup> interpreted many

TABLE VI. Results.

	This work (eV)	Sugar and Reader <sup>a</sup>	Zmbov and Margrave <sup>b</sup>	Hertel <sup>c</sup> (eV)
Eu	$5.664 \pm 0.008$	$5.68 \pm 0.02$	$5.61 \pm 0.10$	$5.64 \pm 0.05$
Tm	$6.180 \pm 0.008$	$6.18 \pm 0.02$	$5.87 \pm 0.10$	$6.03 \pm 0.04$

<sup>a</sup> J. Reader and J. Sugar, J. Opt. Soc. Am. **56**, 1187 (1966).<sup>b</sup> K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **70**, 3014 (1966).<sup>c</sup> G. Hertel, J. Chem. Phys. **48**, 2053 (1968), contains reference on other earlier surface ionization data.

of the levels arising from the  $4f^{12}6s^25d$  levels of Tm I. These levels start at about  $13\,000\text{ cm}^{-1}$  and go to ca.  $45\,000\text{ cm}^{-1}$ . The  $4f^{12}6s^26d$  levels could then be expected to lie in the region we observed. However, lack of information about the expected series limits of these series makes any interpretation at this point impossible.

Table V lists the observed autoionization lines and their intensity on an arbitrary scale. The low intensity peaks at wavelengths shorter than  $1550\text{ \AA}$  have not been listed.

## CONCLUSIONS

Ionization potentials of europium and thulium have been determined based upon a direct determination by interpretation of photoionization onset. The results are tabulated in Table VI. The agreement between the calculated values of Sugar and Reader<sup>11</sup> and this work is excellent. The surface ionization results of Hertel<sup>12</sup> agree with this work for Eu but the discrepancy for Tm is outside of experimental error. The electron impact of Zmbov and Margrave are expected to be somewhat in error due to autoionization at threshold in Tm and Eu. The normal techniques of deriving thresholds from electron impact data would in the case of

strong resonances near threshold give a smaller value for the ionization potential.

The photoionization of both europium and thulium is dominated by autoionization. Some of the strong lines believed to belong to the core  $+5dnp$  configuration for both europium and thulium have been interpreted and classifications suggested. The interpretation has been primarily based upon Rydberg denominator behavior with the limits derived by taking known states of the ions and adding the experimentally derived ionization potential.

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## Raman Spectrum and Polymorphism of Titanium Dioxide at High Pressures\*

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Raman spectra of the rutile and high-pressure orthorhombic ( $\text{TiO}_2$  II) phases of titanium dioxide have been studied at pressures as high as 40 kbar. The frequency of the  $B_{1g}$  mode of rutile has an unusual negative pressure dependence,  $d\nu/dp = -0.3 \pm 0.1 \text{ cm}^{-1} \cdot \text{kbar}^{-1}$ . Onset of the rutile: $\text{TiO}_2$  II transition is observed at pressures above 26 kbar at room temperature, although the apparent transition pressure and extent of transformation depend upon shear stresses applied to the sample. Shears applied normal to the optic (tetragonal) axis of rutile are most effective for inducing the transition.

This note reports some interesting results of a study of effects of high pressures on the vibrational Raman spectrum of the rutile phase of  $\text{TiO}_2$  and the observation at room temperature and about 26 kbar of the onset of the rutile: $\text{TiO}_2$  II phase transition. Rutile is one of three naturally occurring  $\text{TiO}_2$  polymorphs.<sup>1</sup> It has a tetragonal structure (space group  $D_{4h}^{14}$ ) containing two formula units per primitive cell. Each Ti atom is approximately octahedrally coordinated by oxygens. An unusual aspect of the rutile structure is the oxygen-

oxygen nearest-neighbor distance which is significantly shorter than twice a typical oxygen ionic radius.

A fourth  $\text{TiO}_2$  polymorph (in addition to rutile, anatase, and brookite) has been prepared both by shock-wave compression of rutile<sup>2</sup> and by static compression of rutile at temperatures above 270°C.<sup>3</sup> Previous room-temperature high-pressure experiments gave only erratic indications of only slight conversion of rutile to this high-pressure,  $\text{TiO}_2$  II phase even at pressures as high as 0.18 Mbar.<sup>3</sup> The structure of