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FLUORESCENCE SPECTRA OF URANIUM, NEPTUNIUM, AND CURIUM

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Authors
Conway, John G.
Wallmann, James C.
Cunningham, B.B.
et al.

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John G. Conway, James C. Wallmann, B.B. Cunningham, and George V. Shalimoff

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Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California
September 23, 1957

Fluorescence of AmCl₃ and PuCl₃ in dilute solid solution in a matrix of crystalline anhydrous LaCl₃ has been reported previously.¹,² We have since observed the fluorescence of U⁺³, Np⁺³, and Cm⁺³ in a similar crystalline environment. Observed fluorescence lines and, for Cm⁺³, absorption lines in the region 3000 to 8000 Å are listed in Table I. The fluorescence spectra were obtained by ultraviolet irradiation, as described previously,¹,² although for curium (∼185 μg Cm²⁴⁴ in 183 mg LaCl₃) the radioluminescence is sufficiently intense to be photographed on our 21-foot Wadsworth spectrograph.³ The radioluminescence spectrum, aside from its lower intensity, is identical with that obtained by ultraviolet irradiation. The strong fluorescence group at 4000 Å continued to fluoresce in absorption experiments, and therefore has not been observed as an absorption line by us. It is now known, however, that this appears as a peak in the absorption spectrum of aqueous Cm⁺³.⁴

The fluorescence of NpCl₃ in LaCl₃ was observed at a concentration of ∼0.1 atom % Np²³⁷ similar to the CmCl₃ preparation.

Because of the ready availability of natural uranium, solutions of UC₃ in LaCl₃ up to 20 weight % were prepared.

 Attempts were made to incorporate UC₃ in NaCl, SrCl₂, BiCl₃, and MgCl₂. Although some uranium appeared to dissolve in some of the crystals, none of the products was fluorescent.

Some interpretation of the observed spectra is possible. The ground state of Cm⁺³ is ⁸S₇/₂ with insignificant splitting by the hexagonal crystalline field of LaCl₃, so far as optical spectra are concerned. Multiplet structure therefore arises from crystal-field splittings of excited states. The three-component group of lines at 4600 Å therefore arises from a J = 5/2 level, the four-component group at 4000 Å from a J = 7/2 level, and the two doublets at 3830 Å and 3780 Å from J = 3/2 levels. The group at 4600 Å
probably arises from the $^6P_{5/2}$ level, that at 4000 Å from the $^6P_{7/2}$ level (although it may be the $^6I_{7/2}$), and the two groups with $J = 3/2$ from $^6P$, $^6D$, $^6F$, or $^6G$, or possibly from quartet $S$, $P$, $D$, $F$, or doublet $P$ or $D$, are entering.

The ground state of $\text{Np}^{+3}$ is $^5I_{4}$. A preliminary analysis suggests levels at 60 and 110 cm$^{-1}$ above the ground state. The level of 19870 cm$^{-1}$ is not split and therefore has $J = 0$. The most reasonable assignment for this level is $^5D_{0}$, although $^3P_{0}$ and $^1S_{0}$ are possible.

The doublet at 16070 cm$^{-1}$ is split by 25 cm$^{-1}$. For this $J = 1$ level the possibilities are $^5P$, $^5D$, $^5P$, $^3D$, $^3P$, $^3S$, $^1P$.

The interpretation of the uranium fluorescence spectrum is more difficult than for $\text{Cm}^{+3}$ or $\text{Np}^{+3}$. The splitting of the $^4I_{9/2}$ ground state appears to contain an interval of 180 cm$^{-1}$ followed by a 20 cm$^{-1}$ interval. Absorption-spectra observations suggest that there may be an additional level at about 25 cm$^{-1}$ above ground.

Table I. Spectra of U, Cm, and Np in LaCl$_3$ (wavelength in angstroms)

<table>
<thead>
<tr>
<th></th>
<th>CmCl$_3$ in LaCl$_3$: Fluorescence</th>
<th>UCl$_3$ in LaCl$_3$: Fluorescence</th>
<th>UCl$_3$ in LaCl$_3$: Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4606</td>
<td>6482$^a$,$^b$</td>
<td>3835</td>
</tr>
<tr>
<td></td>
<td>4603</td>
<td>6915$^b$</td>
<td>3830</td>
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<tr>
<td></td>
<td>4588</td>
<td>6898$^b$</td>
<td>3787</td>
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<td>4001</td>
<td>6812$^b$</td>
<td>3776</td>
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<tr>
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<td>6208</td>
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</tr>
</tbody>
</table>

$^a$Fluorescence line appears only at room temperature

$^b$Also appears in absorption
References

3. M. Fred and D.M. Gruen (Argonne National Laboratory) (private communication) have observed this radioluminescence on a fast spectrograph, and confirm our results.