Lawrence Berkeley National Laboratory
Recent Work

Title
OPTICAL PROPERTIES OF TETRAVALENT URANIUM IN THE SOLID STATE

Permalink
https://escholarship.org/uc/item/9q20t7jh

Author
Edelstein, N.

Publication Date
1987-04-01
Optical Properties of Tetravalent Uranium in the Solid State

N. Edelstein
April 1987
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Optical spectra of f\n ions are characterized by intra-configuration transitions which are relatively sharp. For trivalent lanthanide ions diluted in non-interacting host crystals (i.e. Pr\textsuperscript{3+}/LaCl\textsubscript{3}) linewidths obtained by conventional optical spectroscopy techniques are the order of 1 cm\textsuperscript{-1} [1,2]. Tetravalent U\textsuperscript{4+} ions usually have linewidths on the order of 1-10 cm\textsuperscript{-1} [3]. Some U\textsuperscript{4+} ions diluted in Th tetrahalide crystals have peculiar line shapes due to an incommensurate structure of the host crystal. These anomalous results have been thoroughly studied [4].

For f\n ions in sites with inversion symmetry, the zero phonon electronic transition may not be observed. Instead, a zero phonon electronic transition plus one or more vibrational transitions are found. By assigning the vibrational transitions the zero phonon electronic transition may be inferred [5-8].

Once the optical spectra have been obtained, the data are fit to the parameters of a phenomenological Hamiltonian from which a calculated spectrum is obtained. The goodness of fit is determined by the value of \( \sigma \) (in cm\textsuperscript{-1}), the rms deviation, defined as

\[
\sigma = \left[ \frac{1}{n-p} \sum_{i=1}^{n} \left( \frac{E_i(\text{exp}) - E_i(\text{calc})}{E_i(\text{exp})} \right)^2 \right]^{1/2}
\]
where $E_i^{(exp)} - E_i^{(calc)}$ are the $i$th experimental and calculated levels, respectively, $n$ is the number of assigned levels, and $p$ is the number of free parameters [9]. For the trivalent lanthanide ions in $\text{LaCl}_3$, $\sigma \approx 8-20 \text{ cm}^{-1}$, and for the trivalent actinide ions in $\text{LaCl}_3$, $\sigma \approx 20 \text{ cm}^{-1}$.

The magnitude of the crystal field depends strongly on the type of host crystal and the distances of the nearest neighbor ions to the $f^n$ ion. A qualitative measure of the magnitude of the crystal field is provided by the parameter first defined by Auzel [10]:

$$N_y = \left[ \frac{1}{\sqrt{4\pi}} \sum_{k} \left( \frac{E_k^2}{q} \right) \right]^{1/2}.$$

The Table lists $\text{U}^{4+}$ in various host crystals plus, for comparison purposes, $\text{Pr}^{3+}$ or $\text{Nd}^{3+}$ in various crystals and the free ion $\text{U}^{4+}$ [11-22].

There are a number of noteworthy trends in this Table. First of all, the rms deviation $\sigma$ for the $\text{U}^{4+}$ compounds is much worse on the average than found for the $\text{Pr}^{3+}$ or $\text{Nd}^{3+}$ examples. Only in the best case does the $\sigma$ for a $\text{U}^{4+}$ compound approach that of the lanthanide ion. The $\text{U}^{4+}$ organometallic compounds fit poorly. Most of the data available for these compounds are for the low-lying levels and the free ion parameters are not well determined. The centrosymmetric complexes $\text{UCl}_6^{2-}$ and $\text{UBr}_6^{2-}$ have been the subject of intensive studies, and the data appear extremely reliable. Nevertheless, they are among the worst-fitting cases. Similarly, the data for $\text{U}^{4+}/\text{ZrSiO}_4$ is quite extensive, yet the fit is poor.
Finally, there appears to be a correlation between a poor fit and a large value of \( a \). In most cases the fit is worse when the value of the parameter \( N_v / \sqrt{4\pi} \) is large indicating a very strong crystal field.

It is difficult to know how to proceed. Some directions to be tried or already underway are:

- Reexamination of the parametric theory to see if other interactions can be included [23, 24];
- Ab initio calculations of \( U^{4+} \) molecular or cluster systems such as \( U(BH_4)_4 \) or \( UCl_6^{-} \) [25];
- Optical studies of higher atomic number tetravalent ions to determine the systematics of the series [26, 27];
- The use of polarized neutrons to study directly bonding or covalency effects [28].

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Table. Summary of Some $^{4+}$ Optical Data Plus Some Other Systems

<table>
<thead>
<tr>
<th>System</th>
<th>No. Levels</th>
<th>Assigned</th>
<th>$\sigma$ (cm$^{-1}$)</th>
<th>$N_y/\sqrt{4\pi}$ (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{4+}$U/ThBr$_4$</td>
<td>26</td>
<td>36</td>
<td>1544</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>$^{4+}$U/ThCl$_4$</td>
<td>25</td>
<td>46</td>
<td>1560</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>UCl$_4$</td>
<td>26</td>
<td>60</td>
<td>1602</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>$^{4+}$U/ThSiO$_4$</td>
<td>25</td>
<td>71</td>
<td>1617</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>$^{4+}$U/ZrSiO$_4$</td>
<td>30</td>
<td>112</td>
<td>3113</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>U(BD$_4$)$_4$/Hf(BD$_4$)$_4$</td>
<td>19</td>
<td>&gt;52</td>
<td>4346</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>[Cp$_3$U(NCS)$_2$]$^-_4$</td>
<td>18</td>
<td>&gt;250</td>
<td>2923</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>[Cp$_3$U(NCBH$_3$)$_2$]$^-_4$</td>
<td>18</td>
<td>&gt;250</td>
<td>2943</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>UBr$_2^-_6$</td>
<td>26</td>
<td>&gt;225</td>
<td>3167</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>UCl$_2^-_6$</td>
<td>21</td>
<td>&gt;150</td>
<td>3471</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>CP$_3$UCl</td>
<td>27</td>
<td>125</td>
<td>3143</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>PrCl$_2^-_6$</td>
<td>27</td>
<td>14.8</td>
<td>980</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Nd$^{3+}$/LaCl$_3$</td>
<td>10</td>
<td>8.1</td>
<td>300</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>$^{4+}$U (free ion)</td>
<td>13</td>
<td>9.8</td>
<td></td>
<td></td>
<td>22</td>
</tr>
</tbody>
</table>
References


