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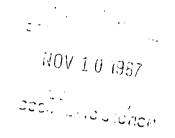
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UNIVERSITY OF CALIFORNIA

# Materials & Chemical Sciences Division

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**Optical Properties of Tetravalent Uranium** in the Solid State

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#### Optical Properties of Tetravalent Uranium in the Solid State

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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.  $Pr^{3+}/LaCl_3$ ) linewidths obtained by conventional optical spectroscopy techniques are the order of 1 cm<sup>-1</sup> [1,2]. Tetravalent U<sup>4+</sup> ions usually have linewidths on the order of 1-10 cm<sup>-1</sup> [3]. Some U<sup>4+</sup> 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<sup>n</sup> 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<sup>-1</sup>), the rms deviation, defined as

 $\sigma = \sum_{i} \left[ \frac{(E_{i}(exp)^{-E_{i}(calc)})^{2}}{n - p} \right]^{1/2}$ 

where  $E_{i(exp)}^{-E}_{i(calc)}$  are the ith 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 LaCl<sub>3</sub>,  $\sigma - 8-20 \text{ cm}^{-1}$ , and for the trivalent actinide ions in LaCl<sub>3</sub>,  $\sigma - 20 \text{ cm}^{-1}$ .

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<sup>n</sup> ion. A qualitative measure of the magnitude of the crystal field is provided by the parameter first defined by Auzel [10]:

$$\frac{N_{v}}{\sqrt{4\pi}} = \left[\sum_{k} \frac{(B_{q}^{k})^{2}}{(2k+1)}\right]^{1/2}$$

The Table lists  $U^{4+}$  in various host crystals plus, for comparison purposes,  $Pr^{3+}$  or  $Nd^{3+}$  in various crystals and the free ion  $U^{4+}$  [11-22]. There are a number of noteworthy trends in this Table. First of all, the rms deviation  $\sigma$  for the  $U^{4+}$  compounds is much worse on the average than found for the  $Pr^{3+}$  or  $Nd^{3+}$  examples. Only in the best case does the  $\sigma$  for a  $U^{4+}$  compound approach that of the lanthanide ion. The  $U^{4+}$  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  $UCl_6^{2-}$  and  $UBr_6^{2-}$ 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  $U^{4+}/ZrSiO_4$  is quite extensive, yet the fit is poor.

Finally, there appears to be a correlation between a poor fit and a large value of  $\sigma$ . In most cases the fit is worse when the value of the parameter  $N_{\rm u}/\sqrt{4\pi}$  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  $UCl_{6}^{2-}$  [25];
  - Optical studies of higher atomic number tetravalent ions to determine the sytematics of the series [26,27];
- The use of polarized neutrons to study directly bonding or covalency effects [28].

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Table. Summary of Some U<sup>4+</sup> Optical Data Plus Some Other Systems

System	No. Levels Assigned	σ (cm <sup>-1</sup> )	$N_v/\sqrt{4\pi} (cm^{-1})$	Ref.
			<u> </u>	·
U <sup>4+</sup> /ThBr <sub>4</sub>	26	36	1544	11
U <sup>4+</sup> /ThCl <sub>4</sub>	25	46	1560	12
UC14	26	60	1602	13
U <sup>4+</sup> /ThSiO <sub>4</sub>	25	71	1617	14
U <sup>4+</sup> /ZrSiO <sub>4</sub>	30	112	3113	15
U(BD <sub>4</sub> ) <sub>4</sub> /Hf(BD <sub>4</sub> ) <sub>4</sub>	19	<b>ب</b> 52	4346	16
[Cp3U(NCS)2]	18	>250	2923	17
[Cp <sub>3</sub> U(NCBH <sub>3</sub> ) <sub>2</sub> ]	18	>250	2943	17
UBr <sub>6</sub> <sup>2-</sup>	26	>225	3167	18
uc1 <sup>2-</sup>	21	>150	3471	18
Cp <sub>3</sub> UC1	27	125	3143	19
PrC1 <sup>2-</sup> 6	27	14.8	980	20
Nd <sup>3+</sup> /LaCl <sub>3</sub>	10	8.1	300	21
U <sup>4+</sup> (free ion)	13	9.8	·	22

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