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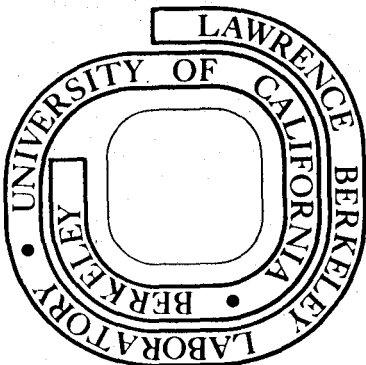
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ABSORPTION AND EMISSION SPECTRA OF U^{4+} DILUTED IN $ThBr_4$
SINGLE CRYSTALS[†]

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ABSTRACT

The absorption and fluorescence spectra of U^{4+} diluted in single crystals of $ThBr_4$ have been measured at room temperature, 77°K, and 4.2°K. The crystal symmetry site of the U^{4+} ion is D_{2d} . Twenty three levels have been assigned and a least-squares fit varying nine parameters (and fixing three parameters) gave a mean energy deviation of 89 cm^{-1} . The values of the parameters obtained from the best fit are (in cm^{-1}), $F^2 = 43770 \pm 797$, $F^4 = 31302 \pm 4200$, $F^6 = 22248 \pm 2425$, $\zeta = 1719 \pm 44$, $\alpha = 36$, $\beta = -600$, $\gamma = 1000$, $B_0^2 = -919 \pm 85$, $B_0^4 = -305 \pm 70$, $B_4^4 = -825 \pm 137$, $B_0^6 = 636 \pm 917$, $B_4^6 = -1937 \pm 202$. There does not appear to be a systematic correlation between the crystal field parameters obtained for U^{4+} in $ThBr_4$ and those reported earlier for U^{4+} in UCl_4 or in $ZrSiO_4$.

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INTRODUCTION

High resolution optical studies of actinide ions have mainly dealt with the tripositive state in order to compare the $5f^n$ spectra directly with their lanthanide analogs. There have been some high resolution studies of tetrapositive actinide ions in O_h symmetry¹⁻³ and further studies of U^{4+} ($5f^2$) in D_{2d} symmetry. The first reported work in the lower symmetry sites was by McLaughlin⁴ who grew a single crystal of UCl_4 and obtained and interpreted its optical spectrum. This work was later reexamined by Hecht and Gruber⁵ who obtained more data and performed a more complete analysis. Richman, Kisliuk, and Wong⁶ studied the absorption spectrum of U^{4+} diluted in $ZrSiO_4$ and their work was later extended and amplified by Mackey, Runciman, and Vance.⁷ In both UCl_4 and $ZrSiO_4$ the local symmetry about the U^{4+} ion was D_{2d} . The spectra obtained consisted of many more lines than could be reasonably attributed to zero phonon electronic transitions.

The diamagnetic material, $ThBr_4$, is a new host material for tetravalent ions with an optical and near infra-red window from 33000 cm^{-1} to 4000 cm^{-1} . The luminescent properties of pure $ThBr_4$ are well characterized and single crystals doped with various ions can easily be grown.⁸⁻¹² $ThBr_4$ has a tetragonal crystal structure isostructural with UCl_4 ^{13,14} which allows the observation of polarized spectra, and its unique axis can easily be obtained by optical methods. The Th^{4+} ion is at a site of D_{2d} symmetry and presumably tetrapositive actinide ions will substitute in these sites. It has also been shown that impurity ions show greater fluorescence in bromide hosts than in oxide or chloride materials.¹⁵ We report in this paper preliminary

results on the absorption and emission spectrum of U^{4+} diluted in $ThBr_4$. This work represents the first report of the fluorescence spectrum of U^{4+} .

EXPERIMENTAL

The crystals were grown at Orsay. The $ThBr_4$ was prepared by the direct reaction of thorium metal and bromine at $950^\circ C$ in a quartz apparatus. Because $ThBr_4$ is very hygroscopic, all the handling was done in a metal glove box under nitrogen atmosphere. Single crystals of $ThBr_4$ to which UBr_4 had been added in a small concentration were grown by the Bridgman method. The crystals were about 0.5 cm^3 in volume and were easily cleaved and polished. The orientation when checked optically showed that the unique axis was perpendicular to the cleaved face. After cleaving and polishing, the crystals were sealed in parallel-sided quartz tubes under a pressure of 100 mm Hg of helium. Several crystals 10 mm in length by 5 mm width and 1 mm thick were obtained from a single preparation. For polarization studies a 10 mm by 3 mm by 2 mm sample was prepared.

Several checks were made on the crystal. First, by x-ray diffraction analysis, the host structure was found to be the tetragonal form of $ThBr_4$. Secondly, the doped crystal was dissolved in aqueous solution and the absorption spectrum of the solution was found to be $U^{4+}_{(aq)}$. All the uranium in the doped crystal was not necessarily U^{4+} since U^{3+} would be oxidized on dissolution. However, it seems

unlikely that during the crystal growing process the U^{4+} would reduce to U^{3+} . The dissolution experiment showed no spectra of the pentavalent or hexavalent states of uranium and these ions are therefore less than 1% of the total uranium content. The analysis of this crystal indicates that the dopant concentration was about 0.1%.

For the spectroscopic studies the doped crystals sealed in the quartz tubes were immersed in liquid nitrogen or liquid helium. Preliminary absorption studies were obtained at room temperature, 77°K, and 4.2°K with a Cary 17 spectrophotometer between 4000 and 25000 cm^{-1} . These spectra are shown in Figure 1. Crystals at the same temperatures were photographed on a 3.4 m Ebert spectrograph and on a 0.7 m Ebert spectrograph. The 3.4 m spectrograph was calibrated using an electrodeless lamp of ThI_4 excited by a 2450 MHz discharge. The dispersion was about 5.2 Å/mm. The 0.75 m spectrograph was calibrated with a mercury discharge lamp and the dispersion was about 19 Å/mm.

Intensities were estimated visually with differences in emulsions taken into account by measuring overlapping lines and normalizing the intensities. The lines at wavelengths 10000 Å and longer were obtained from the Cary 17 spectra. Because of the small crystal size only axial spectra could be obtained on the Cary.

All the emission spectra were photographed on the 0.75 m spectrograph. Two methods were employed for obtaining the fluorescence. The first method used a 100 watt Hanovia mercury lamp and dielectric filters for excitation. The 2537 Å filter had a 134 Å half width and

the 3663 Å filter had a 100 Å half width. The second method was to pass the radiation from a 100 watt quartz iodine lamp through a 0.25 m monochromator. The half width was 160 Å. The monochromator was set to the absorption peaks of the spectrum.

RESULTS AND DISCUSSION

The calculated energy levels were obtained by direct diagonalization of the electrostatic, spin-orbit, and crystal field Hamiltonians¹⁶

$$H = H_1 + H_2 + H_3;$$

$$H_1 = \sum_{i>j=1}^N \frac{e^2}{r_{ij}}$$

$$H_2 = \sum_{i=1}^N \zeta(r_i) (\tilde{s}_i \cdot \tilde{l}_i)$$

$$H_3 = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_4^4 (C_4^{(4)} + C_{-4}^{(4)}) + B_0^6 C_0^{(6)} + B_4^6 (C_4^{(6)} + C_{-4}^{(6)})$$

The matrix was factored by the crystal field quantum number μ into three submatrices $\mu = 0$, of rank 25, $\mu = \pm 1$, each of rank 21, and $\mu = 2$, of rank 24. The $\mu = 0$ matrix corresponds to the symmetries Γ_1 and Γ_2 , the $\mu = \pm 1$ corresponds to the doubly degenerate state Γ_5 , and the $\mu = 2$ corresponds to the symmetries Γ_3 and Γ_4 . The selection rules for these symmetries are given by Richman et al.⁶ Our matrices were checked by reproducing the calculated energy levels of Hecht and Gruber⁵ and of Mackey, Runciman, and Vance⁷ using their values of the parameters. In

agreement with Mackey et al., we were unable to reproduce the results of Richman, Kisliuk, and Wong.⁶

Following the work of Rajnak¹⁷ we decided to initially vary only the Slater parameter F^2 and the spin-orbit coupling constant ζ , and consequently fixed the ratios of $F^4/F^2 = 0.75$ and $F^6/F^2 = 0.56$. Preliminary values of F^2 and ζ were obtained by picking out the centers of gravity and assigning LSJ values. These levels were then fit varying the free ion parameters F^2 and ζ (maintaining the ratios given earlier). Table 1 shows the preliminary free ion assignments, the calculated values, and the parameter values. The configuration interaction parameters α , β , and γ were fixed at the values found for $\text{Np}^{3+}:\text{LaCl}_3$ ¹⁸ except that α was varied in the later free ion fittings. The free ion assignments made were for the most part in the same order as obtained by Hecht and Gruber⁵ and by Richman, Kisliuk, and Wong.⁶ We found the three states 3P_0 , 1D_2 , and 1G_4 were very close in energy and consequently, when the crystal field interaction was included, would be badly mixed.

There were many more lines observed in the spectrum than could possibly be due to zero phonon lines of the $5f^2$ configuration. No constant differences could be found in the complete line list. We have arbitrarily chosen lines with an intensity above 2 (on a scale of 1-10) and have listed the lines obtained at 4.2°K and their polarizations in Table 2. There was only one temperature dependent line observed which is noted in Table 2. We assumed the ground state to be a Γ_4 state as found previously⁵⁻⁷ and assigned a number of transitions which appeared fairly certain. The free ion parameters were fixed at

the values obtained earlier, the crystal field parameters were adjusted for the best fit. More transitions were assigned, the crystal field parameters adjusted, and finally all the free ion parameters (except α , β , γ) and the crystal field parameters were allowed to vary simultaneously. We assigned 23 levels and obtained a mean energy deviation of 89 cm^{-1} . The assignments and calculated energy levels are also given in Table 2. In Table 3 we list the values of the parameters obtained for U^{4+} in UCl_4 , ZrSiO_4 , and in ThBr_4 .

The free ion parameters we obtained appear to be in line with Hartree-Fock calculations and empirical correlations done by Rajnak.¹⁷ However, the crystal field parameters found are very tentative, and for B_0^6 even the sign of the parameter is in doubt. There does not appear to be any systematic trend for the values of the parameters for U^{4+} in D_{2d} symmetry for the three crystals studied.

The fluorescence spectrum of U^{4+} has been observed for the first time. These emission lines are strongly dependent on temperature and the energy of the exciting radiation. At room temperature there is no fluorescence while at 77°K only three broad features occur at 5190 \AA , 6000 \AA , and 6980 \AA with excitation by the 3663 \AA Hg line. At 4.2°K these bands are fully resolved into many lines as listed in Table 4. The 2537 \AA Hg line did not produce fluorescence even though there is a strong absorption band of ThBr_4 at this frequency. The results of some selective excitation experiments at 4.2°K are given in Table 5. When the crystal was slowly heated from 77°K to room

temperature while being excited by the 3663 Å line, the fluorescence disappeared between 100°K - 125°K.

Two emission lines correspond to transitions observed in the absorption spectrum. From our assignments the emission line at 6965 Å (u) corresponds to a transition from the 3P_0 to the 3H_4 ground state and the line at 5183 Å (a) corresponds to a transition from the 1I_6 to the 3H_4 . Selective excitation of this band at ~5100 Å causes transitions to two groups of levels, the ground term 3H_4 and another group approximately 4000 cm^{-1} higher in energy. These emission data locate the first excited electronic term which we have assigned to the 3F_2 and which has been listed in Table 2 and used in fitting energy levels. Again as in the absorption spectrum there are many more lines in the emission spectrum than can be reasonably assigned to zero phonon bands of the $5f^2$ configuration.

SUMMARY

We have measured the absorption and fluorescence spectrum of U^{4+} diluted in ThBr_4 . The strong lines in the absorption spectrum have been assigned and the electrostatic, spin-orbit, and crystal field parameters have been obtained from a least-squares fit of the calculated levels to the measured levels. There appears to be no systematic correlation of the crystal field parameters obtained in this work to those reported earlier for U^{4+} in UCl_4 and ZrSiO_4 .

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Table 1. Observed and calculated free ion values for $U^{4+}:\text{ThBr}_4$. The observed free ion values were found by estimating the centers of the multiplets from this spectra.

Observed (cm^{-1})	Calculated ^a (cm^{-1})	Obs.-Calc. (cm^{-1})	Assign.
600	652	52	3H_4
4068.6	4069	0	3F_2
6075	6101	26	3H_5
8510	8319	-191	3F_3
--	8655	--	3F_4
10678	10783	105	3H_6
14366	14472	106	3P_0
14792	14700	-92	1D_2
14996	14967	-29	1G_4
17350	17066	-284	3P_1
19510	19875	365	1I_6
21799	21741	-58	3P_2
--	37175	--	1S_0

^a Calculated with $F^2 = 44007.9 \text{ cm}^{-1}$, $\zeta = 1736.7 \text{ cm}^{-1}$ and F^4 and F^6 as given by the ratios in the text, $\alpha = 36 \text{ cm}^{-1}$, $\beta = -600 \text{ cm}^{-1}$, $\gamma = 1000 \text{ cm}^{-1}$.

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
3H_4	252	4	0			
3H_4	314	5				
3H_4	341	1				
3H_4	631	5				
3H_4	722	3				
3H_4	779	2				
3H_4	791	1				
3F_2	3780	3				
3F_2	3912	4				
3F_2	4012	5	4068 ^e		--	
3F_2	4067	1				
			5724	17467	8	α
3H_5	5699	5	5729	17450	8	α
3H_5	5745	2				
			5772	17320	3	α

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
3H_5	5773	3				
3H_5	6034	2				
3H_5	6057	5	6326	15800	5	α
3H_5	6099	1				
3H_5	6138	4				
3H_5	6318	5	6425	15560	3	α
			6475	15440	3	α
3F_3	8038	4				
3F_3	8073	5				
3F_3	8265	5				
$^3F_4, ^1G_4$	8272	1				
3F_3	8288	3				
$^3F_4, ^1G_4$	8338	4				
3F_3	8339	2				
$^3F_3, ^3F_4, ^1G_4$	8437	5	8473	11800	8	α

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
$^3F_4, ^1G_4$	8445	3				
$^3F_4, ^1G_4$	8542	5	8547	11700	10	α
$^3F_4, ^1G_4, ^3F_3$	8563	2				
$^3F_4, ^1G_4$	8621	1				
			9530	10490	6	α
3H_6	10224	4				
3H_6	10287	5				
3H_6	10402	1				
3H_6	10629	1				
3H_6	10674	2				
3H_6	10687	5	10658	9380	3	α
3H_6	10700	3				
3H_6	10867	5	10697	9345	2	α
3H_6	11119	4				

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
3H_6	11265	3				
			14022 ^f	6990	--	$\alpha\sigma$
$^3F_4, ^1G_4$	14335	1	14366	6959	8w	Π
$^1D_2, ^3P_2$	14408	3				
$^3P_2, ^1D_2$	14416	4				
$^1D_2, ^3P_2$	14466	5	14354	6965	7	$\alpha\sigma$
3P_0	14493	1	14477	6905	5w	Π
$^3F_4, ^1G_4$	14561	3				
			14603	6847	4	Π
			14612	6842	4	Π
$^3F_4, ^1G_4$	14724	2				
$^3F_4, ^1G_4$	14729	5	14661	6819	10vw	$\alpha\sigma$
$^3F_4, ^1G_4$	14765	4				
			14765	6771	4w	Π

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
$1D_2, 3P_2, 3P_0$	14801	1	14820	6736	8vw	Π
$3F_4, 1G_4$	14849	5	14923	6699	10vw	Π
			15020	6656	8w	Π
$1G_4, 3F_4$	15200	1	15202	6576	6vw	Π
			15423	6482	5	Π
			16003	6247	8sh	$\alpha\sigma$
			16016	6242	10	Π
$3P_1$	17022	2	17338	5766	4	Π
$3P_1$	17293	5	17342	5765	9	$\alpha\sigma$
			17369	5756	8sh	$\alpha\sigma$
$1I_6$	19095	3				
$1I_6$	19137	5	19292	5182	6	$\alpha\sigma$
$1I_6$	19176	1	19303	5179	6	Π

00004710594

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

Calculated			Experimental			
L-S State ^a	Energy (cm^{-1})	Irreduc. Repr.	Energy (cm^{-1})	Wavelength ^b (\AA)	Intensity ^c	Polarization ^d
			19318	5175	8	$\alpha\sigma$
			19446	5141	4w	Π
$1I_6$	19538	4				
$1I_6$	19603	5	19335	5170	10sh	$\alpha\sigma$
$1I_6$	19707	2				
$1I_6$	19811	1	19935	5014	4	Π
$1I_6$	19949	5	19942	5013	8	$\alpha\sigma$
$1I_6$	20148	3				
$1I_6$	20149	4				
$3P_2, 1D_2$	21339	3				
$3P_2, 1D_2$	21635	4				
$3P_2, 1D_2$	21812	1	21761	4594	8sh	Π
$3P_2, 1D_2$	21896	5	21837	4578	7sh	$\alpha\sigma$
$1S_0$	36135	1				

Table 2. Absorption Spectrum of $U^{4+}:\text{ThBr}_4$ (Cont'd)

^aThe principal components are listed in order of importance.

^bWavelength in air.

^cIntensities are estimated visually. A normalization was made for different emulsions and the Cary 17 by the comparison of overlapping lines. Most intense line -10; sh-sharp line, width less than 5 Å; w-wide; vw-very wide.

^d Π - Π polarization, σ - σ polarization, α axial spectrum.

^eFrom the fluorescence data.

^fTemperature dependent line, not at 4.2°K, intensity ~4 at 77°K.

Table 3. Parameters for the U^{4+} ion in various crystals

Crystal	UCl_4^a	$ZrSiO_4^b$	$ThBr_4^c$
F^{2d}	38835	44257	43770 ± 797
F^4	42242	40293	31302 ± 4200
F^6	18883	31287	22248 ± 2425
ζ	1666	1740	1719 ± 44
α	--	22.8	36
β	--	--	-600
γ	--	--	1000
B_0^2	-582	-2000	-919 ± 85
B_0^4	-3027	2000	-305 ± 70
B_4^{4e}	-5680	5125	-825 ± 137
B_0^6	-2262	-5792	636 ± 917
B_4^{6e}	795	-428	-1937 ± 202

^aReference 5.

^bReference 7.

^cThis work, mean energy deviation for 23 levels is 89 cm^{-1} . The errors represent values for the parameters which increase the mean deviation by 5 cm^{-1} .

^dAll units are cm^{-1} .

^eThe signs of both B_4^4 and B_4^6 may be changed simultaneously without changing the calculated energies. See reference 6.

Table 4. Emission spectrum of $U^{4+}:\text{ThBr}_4$ at 4.2°K with excitation by the 3663 \AA Hg line.

Exposure Times					
15 minutes			5 hours		
	Wavelength (\AA)	Energy (cm^{-1})	Comments ¹	Wavelength (\AA)	Energy (cm^{-1})
a	5182	19292	} str.br. ² br. str.shp.	5171	19333 ²
b	5198	19233			
c	5203	19214	wk.		
d	5213	19177	str.br.		
e	5222	19144	shp.		
f	5231	19111	shld.		
g	5239	19082	str.br.		
h	5270	18970	wk.shp.		
i	5289	18909	wk.br.		
				5313	18817
				5366	18636
				5372	18610
j	5444	18364	str.shp.		
k	5454	18330	str.shp.		
				5478	18250
				5487	18226
				5509	18147
				5563	17971

Table 4. Emission spectrum of $U^{4+}:\text{ThBr}_4$ at 4.2°K with excitation by the 3663 Å Hg line. (Cont'd)

Exposure Times				
15 minutes			5 hours	
Wavelength (Å)	Energy (cm^{-1})	Comments ¹	Wavelength (Å)	Energy (cm^{-1})
			5754	17374
			5760	17356
			5852	17083
			5883	16993
			5934	16847
l	5913	16907 med.	5957	16782
			6177	16185
			6236	16032
			6360	15719
m	6440	15524 wk. shp.	6454	15496
			6509	15359
			6519	15335
n	6573	15210 str.br.		
o	6582	15189 shld.		
p	6587	15177		
q	6611	15122		
r	6622	15097 wk.br.		

Table 4. Emission spectrum of $U^{4+}:\text{ThBr}_4$ at 4.2°K with excitation by the 3663 Å Hg line. (Cont'd)

Exposure Times				
15 minutes			5 hours	
Wavelength (Å)	Energy (cm^{-1})	Comments ¹	Wavelength (Å)	Energy (cm^{-1})
			6729	14857
			6850	14594
			6887	14516
			6914	14459
			6932	14422
s	6941	14403		
t	6958	14368		
u	6965 ³	14354		
v	6996	14290		
w	7021	14239		
x	7029	14223		
y	7036	14209		
			7051	14178
z	7068	14144		

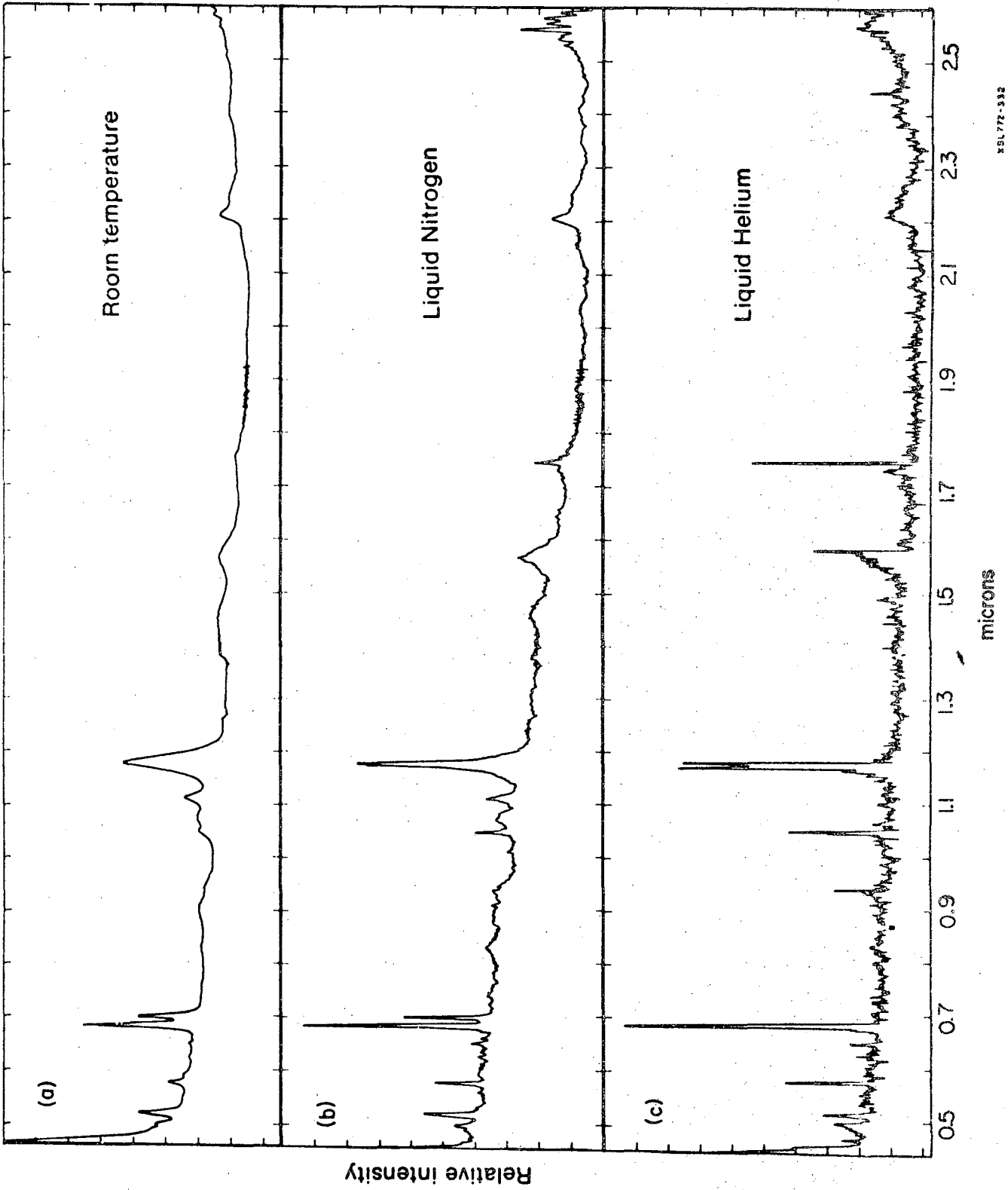
1. b. band; br. broad (linewidth $> 8 \text{ \AA}$); shld. shoulder; shp sharp (linewidth $\sim 3\text{-}5 \text{ \AA}$); str. strong; med. medium; wk. weak.
2. Seen in absorption.
3. The high wavelength edge coincides with an absorption line. The absorption line is about 1 \AA wide compared to this fluorescence feature which is 31 \AA wide.

Table 5. Selective excitation spectrum of $\text{ThBr}_4:\text{U}^{4+}$ at 4.2°K

Excitation Wavelength (Å)		Emission Lines (Å)	Comments
2537	Hg lamp + filter	no fluorescence	
3663	Hg lamp + filter	fluorescence spectrum of Table 4	
4590	{ 4510 4670 Quartz iodine lamp + monochromator	no fluorescence	
4850	{ 4770 4930 Quartz iodine lamp + monochromator	a,b,d,e,g,j,k, m,n,p,q,r	} weak
5000	{ 4920 5080 Quartz iodine lamp + monochromator	a to i j,k,m n to r	} strong
5160	{ 5080 5240 Quartz iodine lamp + monochromator	u	} very weak
5750	{ 5670 5830 Quartz iodine lamp + monochromator	5883, l, +band 5934 5957 +band 6360 u,v,w,	} weak strong

FIGURE CAPTION

Figure 1. Absorption spectra of $U^{4+}:\text{ThBr}_4$ at various temperatures.



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