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Optical Properties of U^{4+} in α-$ThBr_4$*

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Thorium tetrahalides (X = Cl, Br) have two polymorphic forms [1] with a transformation temperature of 426 °C for the tetrabromide and 405 °C for the tetrachloride. While the space group symmetry of the high temperature form β-$ThBr_4$ is $I4_1/amd$, in which Th^{4+} is at a site of D_{2d} symmetry (above 90 K), the low temperature form α-$ThBr_4$ has a scheelite structure $I4_1/a$ in which the site symmetry of Th^{4+} is S_4. In contrast to β-$ThBr_4$, which undergoes a phase transition below 90 K [2], we verified by Raman scattering and nuclear quadrupole resonance that α-$ThBr_4$ keeps the same structure from room temperature down to 4.2 K.

Recently, a single crystal of α-$ThBr_4$ doped with U^{4+} has been grown and spectroscopic properties of tetravalent uranium have been studied using absorption and emission measurements and Zeeman effect studies. Numerous and very strong fluorescences from U^{4+} in the visible, as well as in the near-infrared and infrared, have been observed for the first time [3] and parameters describing spin-orbit and crystal-field interactions were adjusted with 30 levels using a least-squares minimization procedure in the D_{2d} point group approximation.

Experimental

Samples used in this study were obtained by the Bridgman method as single crystals of α-$ThBr_4$ doped with 20 ppm of U^{4+}. As it is difficult to get the α-form by this method, it was also possible to transform U^{4+} doped β-$ThBr_4$ single crystals to the α-form by heating at 400 °C for several days. In this way the new form becomes polycrystalline.

The absorption and emission spectra in the visible and infrared were measured at different temperatures ranging from 4.2 K to 300 K, with the crystal excited by the full light emission produced by a 24 W iodine lamp, using a Jobin–Yvon HR 1000 high resolution spectrometer.

The selective excitation experiments were performed using a pulsed Sopra tunable dye laser with a Sopra nitrogen laser.

Zeeman splittings were recorded in the visible region at 4.2 K with the crystal in a magnetic field of 6 T.

Results and Discussion

Figure 1 shows the absorption and emission spectra of tetravalent uranium in α-$ThBr_4$ in the visible and IR region at 4.2 K. Since the absorption lines were clearly polarized, we did not attempt to observe any polarization on the emission lines. In contrast to β-$ThBr_4/U^{4+}$, which is incommensurate below 90 K [4], the absorption lines in α-$ThBr_4/U^{4+}$ are very sharp and some of them present phonon sideband structure on the high energy side below 200 cm^{-1}, which indicates strong coupling between the electronic and vibronic states, as in the d elements. The spectra have been interpreted under the assumption that D_{2d} is a good approximation for S_4 symmetry and that the ground state is Γ_4 as for U^{4+} in β-$ThBr_4$ [5]. From the number of lines observed for π and σ polarization, compared to the predicted number of lines using the electric dipole selection rules in D_{2d} and S_4 symmetry, we assumed that D_{2d} is a good approximation [3]. Furthermore, the transition $\Gamma_4 \rightarrow \Gamma_2$, forbidden in D_{2d} symmetry and allowed in S_4 symmetry, particularly the $^3P_1$ (Γ_2) level, is not observed in the π absorption spectra. By comparing the spectra with those of U^{4+} in β-$ThBr_4$, most of the lines could be assigned as $\Gamma_4 \rightarrow \Gamma_1$ transitions for π polarization and $\Gamma_4 \rightarrow \Gamma_5$ transitions for σ polarization. The absorption and emission level assignment has been described elsewhere [3]. The U^{4+}/α-$ThBr_4$ spectrum at higher temperature could be interpreted by absorption from a level at 110 cm^{-1} above the ground state and all the intense emission lines observed could be assigned as transitions coming from excited levels to $^3H_4$ Stark levels which we calculated to be at 110, 473, 623 and 830 cm^{-1}, the first and the last one being assigned as the Γ_5 level. The Zeeman experiments permit clear observation of the splitting of the $^3P_1$ (Γ_5) level and the $^3H_4$ (Γ_5) level at 110 cm^{-1}.

30 levels were fitted by simultaneous diagonalization of the free ion H_o and crystal field Hamiltonian $\mathcal{H}_{cc}$ describing the energy levels of U^{4+} in D_{2d} symmetry. H_o is characterized by the parameters of interelectronic repulsion F^k ($k = 2, 4, 6$), spin-orbit coupling ζ, configuration interaction α, β, γ, and additional parameters P^k ($k = 2, 4, 6$) and M^k ($k = 0, 2, 4$) taking into account finer effects. $\mathcal{H}_{cc}$ is parameterized by the crystal field parameters B^2_0,

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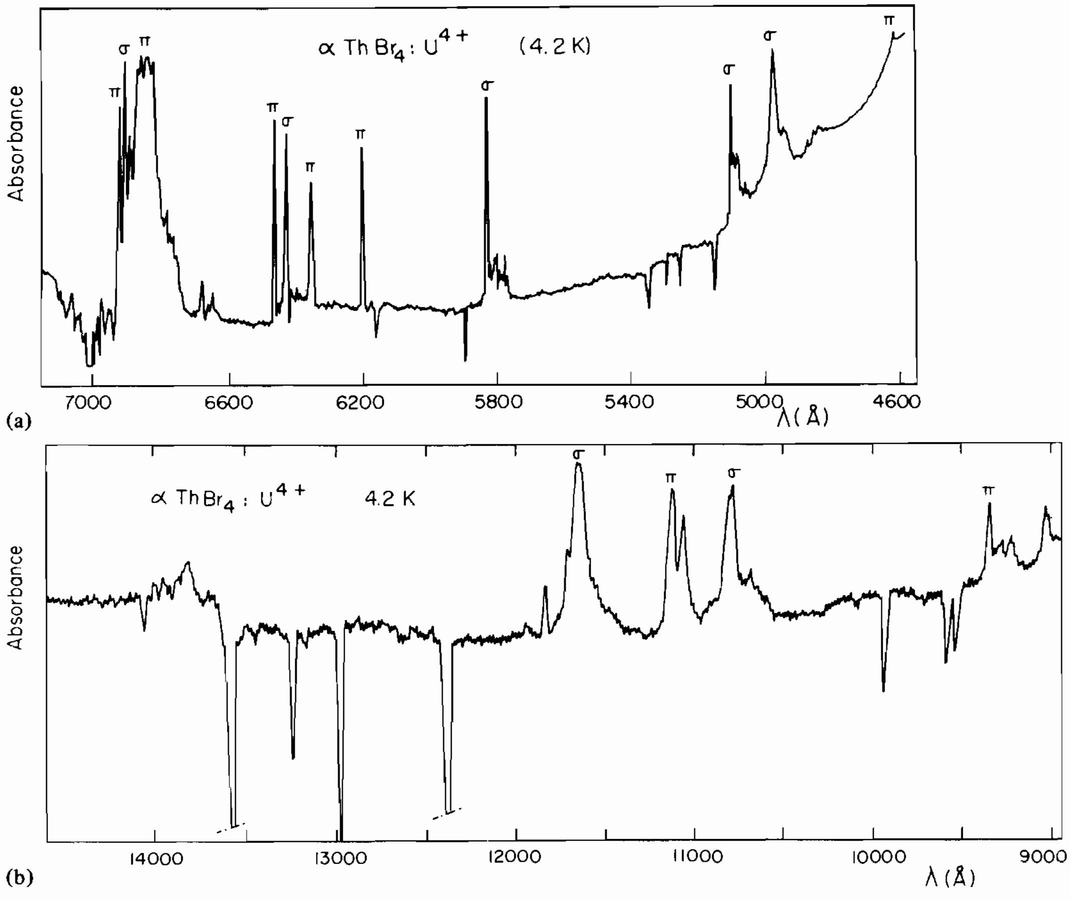

Fig. 1. Absorption and emission spectra of U^{4+}/α-ThBr$_4$ in the visible and infrared region at 4.2 K.

B^4_0, B^4_4, B^6_0 and B^6_4. Fitting the experimental levels with the parameters obtained for β-ThBr$_4$/U^{4+} gave a large r.m.s. deviation for α-ThBr$_4$/U^{4+}. Only $B^2_0 \sim -400$ cm^{-1} gave the correct separation between the $^3P_1$ Γ_2 and Γ_5 levels. With this B^2_0 value, we tried to fit separately the Γ_1 and Γ_5 levels. Finally, the best fit for the 30 levels together was obtained with the starting value calculated with the Γ_1 levels. Our final analysis based upon 30 assigned levels led to a r.m.s. deviation of 77 cm^{-1}. The best fit parameters are listed in Table I along with those of β-ThBr$_4$:U^{4+}. Compared with the spectroscopic parameters obtained for U^{4+} in β-ThBr$_4$ [5] and ThSiO$_4$ [6], the calculated parameters of U^{4+}/α-ThBr$_4$ are very different, particularly B^2_0 which is smaller and the sign of B^4_0 which is negative. If the r.m.s. deviation is not as good as for β-ThBr$_4$, the crystal field parameters are however calculated with an error of about 10%, except for B^6_0 which is determined at 20%.

Tha Auzel parameter [7] N_v can be introduced to give a relative measurement of the crystal field.

$$\frac{N_v}{\sqrt{(4\pi)}} = \left(\sum_{k,q} \frac{1}{2k+1} (B^k_q)^2 \right)^{1/2}$$

Although the parameters are very different from the β-form, the crystal field strength has the same order of magnitude. Moreover, a marked decrease in the F^k parameters, especially for F^4, is observed.

Our results can be compared to those calculated by the covalo-electrostatic method [8] (Table II).

The calculated crystal field parameters are different for the two forms α- and β-ThBr$_4$. For U^{4+} in α-ThBr$_4$, the main discrepancy occurs for B^4_0, while in β-ThBr$_4$ it is for B^6_0. Although the general structure of α-ThBr$_4$ is quite similar to that of β-ThBr$_4$, the major difference between the two forms is the relative orientation of the coordination polyhedra within the structure. In the β-form, the axes of the polyhedron lie in the (100) planes of the unit cell, while in the α-structure the polyhedron has been rotated about 45°, the c axis and the polyhedron axes lying somewhat outside the (110) planes. This rotation allows for a more efficient packing of the Br$^-$ atoms in the α-form. Moreover, the metal–ligand distances are approximately all the same for α-ThBr$_4$, while there are two different Th–Br bond distances for β-ThBr$_4$. The angles in the polyhedra are also different for both forms. This can explain the

TABLE I. Spectroscopic Parameters for U^{4+} in α-$ThBr_4$ in Comparison with those of β-$ThBr_4$ and $ThSiO_4$

Spectroscopic[a] parameters	α-$ThBr_4$:U^{4+}	β-$ThBr_4$:U^{4+}[b]	$ThSiO_4$:U^{4+}[c]
F^2	41529 (158)	42253 (127)	43110 (245)
F^4	36114 (486)	40458 (489)	40929 (199)
F^6	23953 (415)	25881 (383)	23834 (639)
F^4/F^2	0.87	0.96	0.95
F^6/F^2	0.57	0.61	0.55
ζ	1753 (7)	1783 (7)	1840 (2)
α	32 (1)	31 (1)	32.3 (0.4)
β	−644 (144)	−644 (75)	−663 (144)
γ	1200	1200	1200
B^2_0	−382 (73)	−1096 (80)	−1003 (127)
B^4_0	−3262 (197)	1316 (146)	1147 (281)
B^4_4	−1734 (164)	−2230 (85)	−2698 (251)
B^6_0	−851 (334)	−3170 (379)	−2889 (557)
B^6_4	−1828 (163)	686 (246)	−208 (333)
r.m.s.	77	36	71
N'_v	1565	1543	1617

[a]The M^k and P^k values were fixed: $M^0 = 0.99$, $M^2 = 0.55$, $M^4 = 0.38$; $P^2 = P^4 = P^6 = 500$. [b]From ref. 5. [c]From ref. 6.

discrepancy in the values of the spectroscopic parameters for U^{4+} between α- and β-$ThBr_4$ and, in particular, of the crystal field parameters, which are found to be alike in the calculated values, taking into account the covalo-electrostatic method.

TABLE II. Calculated and Experimental Crystal Field Parameters of U^{4+} in α and β-$ThBr_4$ (cm^{-1})

	α-$ThBr_4$		β-$ThBr_4$	
	Covalo-electrostatic method[a]	Experimental	Covalo-electrostatic method[a]	Experimental
B^2_0	−44	−382	−594	−1096
B^4_0	−356	−3262	1298	1316
B^4_4	−1783	−1734	−2527	−2230
B^6_0	−11	−851	−388	−3170
B^6_4	−1040	−1828	145	686

[a]From ref. 8.

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