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Crystal-field analysis of low-temperature UCl_3 and UBr_3 absorption spectra

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Abstract

High-resolution absorption spectra of thin films of UCl_3 and UBr_3 have been measured at 4.2 K in the 4000–30 000 cm^{-1} range. The determined crystal-field lines were used in a computational analysis employing free-ion operators, one-electron crystal-field operators as well as two-particle correlation crystal-field operators. The performed analysis enabled the determination of the Hamiltonian parameters and an unambiguous assignment of 57 and 46 crystal-field levels with a mean error of 31 cm^{-1} for UCl_3 and UBr_3 , respectively.

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Keywords: Uranium trichloride; Uranium tribromide; Low temperature absorption spectra; Crystal-field parameters; Correlation crystal-field parameters; Energy levels.

1. Introduction

Since the first crystal-field analysis of $\text{U}^{3+}:\text{LaCl}_3$ single crystals in 1980 [1] and 1989 [2] further analyses of uranium(III) systems were reported only in recent years for U^{3+} doped LiYF_4 [3], RbY_2Cl_7 [4], $\text{Cs}_2\text{NaYCl}_6$ [5], $\text{Cs}_2\text{LiYCl}_6$ [5] and K_2UX_5 ($X = \text{Cl}, \text{Br}$ or I) [6] single crystals as well as for some polycrystalline samples [7–9]. A detailed analyses of line intensities associated with transitions between individual Stark levels in $\text{U}^{3+}:\text{LaCl}_3$ [10] single crystals have also been presented. Somewhat surprisingly, a spectrum analyses for such basic compounds as the uranium trihalides, except of $\text{U}^{3+}:\text{LaCl}_3$, have not been reported so far.

This paper presents the first crystal-field analysis of non-diluted UCl_3 and UBr_3 samples. The analysis has been carried out with inclusion of selected correlation crystal-field operators. Besides a number of lanthanide ions, such investigations have been hitherto executed for U^{3+} doped LaCl_3 [10] single crystals only.

2. Experimental

Uranium trichloride and tribromide were prepared according to the procedures reported in Refs. [11] and [12], respectively. The electronic absorption spectra of thin films of the compounds (Figs. 1 and 2) were recorded on a Cary 5 NIR–Vis–UV spectrophotometer in the 4000–30 000 cm^{-1} range at 300 and 4.2 K using an Oxford Instruments Model CF1204 cryostat. In order to obtain the spectrum a well ground mixture of the compound with some chlorinated naphthalene oil (index of refraction 1.635) was placed between two quartz windows, approximately 0.8 cm in diameter, pressed to obtain a transparent layer and placed in the cell compartment.

3. Energy level calculations

UCl_3 and UBr_3 are isostructural and crystallize in the hexagonal system, (space group $P6_3/m$, No.176) which consists of $[\text{UX}_9]$ polyhedra formed by trigonal prisms capped on each rectangular face. The crystal field splits the atomic states of the $5f^3$ configuration into Kramers doublets which are classified by the $E_{1/2}$ ($\Gamma_7 + \Gamma_8$), $E_{3/2}$

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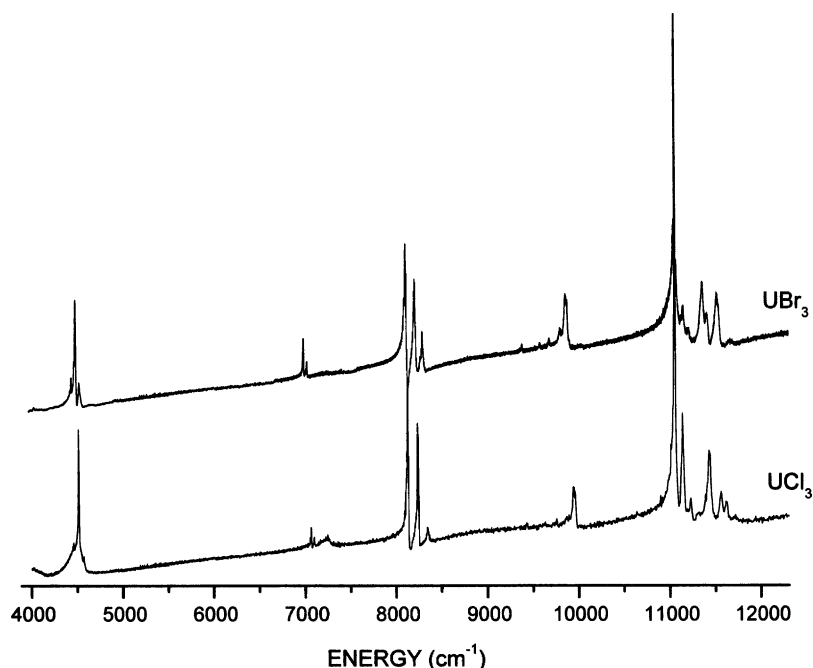


Fig. 1. Absorption spectra of UCl_3 and UBr_3 at 4.2 K in the $4000\text{--}12000\text{ cm}^{-1}$ range showing the red shift of the $5f^3 \rightarrow 5f^3$ bands of UBr_3 .

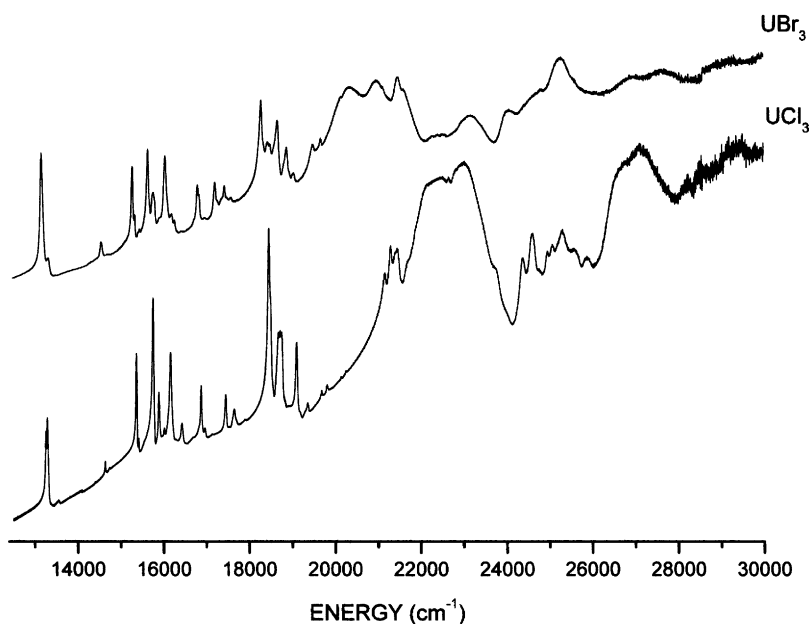


Fig. 2. Absorption spectra of UCl_3 and UBr_3 at 4.2 K in the $12000\text{--}30000\text{ cm}^{-1}$ range showing the appearance of the first strong $5f^3 \rightarrow 5f^2 6d^1$ bands at 21300 and 20300 cm^{-1} , respectively.

($\Gamma_{11} + \Gamma_{12}$) or $E_{5/2}$ ($\Gamma_9 + \Gamma_{10}$) symmetry of the C_{3h} double-rotation group. In the assignment of the recorded crystal-field bands we have followed the results derived from low-temperature σ - and π -polarized absorption spectra of the isostructural $\text{U}^{3+}:\text{LaCl}_3$ single crystals [10]. The selection rules for this symmetry allow one an unambiguous assignment of irrep labels of all lines observed in the spectra.

The crystal-field calculations have been performed by applying the f -shell empirical program for the effective operator model [13] written by M. Reid (University of Canterbury, New Zealand) and running on PC under the Linux Mandrake operating system.

The eigenvectors and eigenvalues of the crystal-field levels were obtained by diagonalization of the combined free-ion and crystal-field energy matrices. The complete

Hamiltonian includes the following terms:

$$\hat{H} = \hat{H}_A + \hat{H}_{CF} + \hat{H}_{CCF}, \quad (1)$$

\hat{H}_A contains the isotropic (atomic) parts of \hat{H} and is defined as

$$\begin{aligned} \hat{H}_A = & E_{ave} + \sum_{k=0,2,4,6} F^k(nf, nf) \hat{f}_k + \zeta_{5f} \hat{A}_{SO} \\ & + \alpha \hat{L}(\hat{L} + 1) + \beta \hat{G}(G_2) + \gamma \hat{R}(R_7) \\ & + \sum_{i=2,3,4,6,7,8} T^i \hat{t}_i + \sum_j M^j \hat{m}_j + \sum_k P^k \hat{p}_k, \end{aligned} \quad (2)$$

where E_{ave} is the spherically symmetric one-electron part of the Hamiltonian, $F^k(nf, nf)$ and ζ_{5f} represent, respectively the radial parts of the electrostatic and spin-orbit interactions, while \hat{f}_k and \hat{A}_{SO} are the angular parts of these interactions. The α , β and γ parameters are associated with the two-body correction terms. $\hat{G}(G_2)$ and $\hat{R}(R_7)$ are Casimir operators for the G_2 and R_7 groups. L is the total orbital angular momentum. The three-particle configuration interaction is expressed by $T^i \hat{t}_i$ ($i=2,3,4,6,7,8$), where T^i are parameters and \hat{t}_i are three-particle operators. The electrostatically correlated spin-orbit perturbation is represented by the P^k parameters and those of the spin-spin and spin-other-orbit relativistic corrections by the M^j parameters. The operators associated with these parameters are designated by \hat{m}_j and \hat{p}_k , respectively. The \hat{H}_{CF} term of the Hamiltonian represents the one electron crystal-field interactions and is defined as

$$\hat{H}_{CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i), \quad (3)$$

where $C_q^{(k)}(i)$ is a spherical tensor of rank k and B_q^k are crystal-field parameters. For the C_{3h} symmetry the

crystal-field Hamiltonian is expressed as follows [14]:

$$\begin{aligned} H_{CF} = & B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_6^6 (C_{-6}^6 + C_6^6) \\ & + B_6^6 i (C_{-6}^6 - C_6^6). \end{aligned} \quad (4)$$

In the coordinate system chosen for the present analysis, the imaginary part of B_6^6 vanishes. The last term of the complete Hamiltonian represents the correlated two-electron crystal-field interactions. Following Reid [14] the parameterization of these interactions may be written in Judd's [15] notation as a set of G_{iQ}^K parameters:

$$\hat{H}_{CCF} = \sum_{i,K,Q} G_{iQ}^K \hat{g}_{iQ}^{(K)}, \quad (5)$$

where i distinguishes the appropriate $\hat{g}_{iQ}^{(K)}$ operator, K runs through the even integers from 0 to 12, and Q is restricted by the crystal-field symmetry.

Since there are 41 independent CCF parameters it was not possible to include all of them in a fit with a relatively small set of experimental data. We have checked the influence of all these parameters and have found that only three $G_{10A,0}^4$, $G_{10B,0}^4$ and $G_{2,0}^4$ fourth-rank parameters and one $G_{10B,0}^6$ sixth-rank parameter are statistically significant for the analysis of the UCl_3 and UBr_3 spectra.

4. Results and discussion

The low-temperature absorption spectra of the UCl_3 and UBr_3 polycrystalline samples exhibit the characteristic for uranium(3+) $5f^3 \rightarrow 5f^3$ transition bands in the 4000–21310 cm^{-1} and 4000–19 694 cm^{-1} absorption

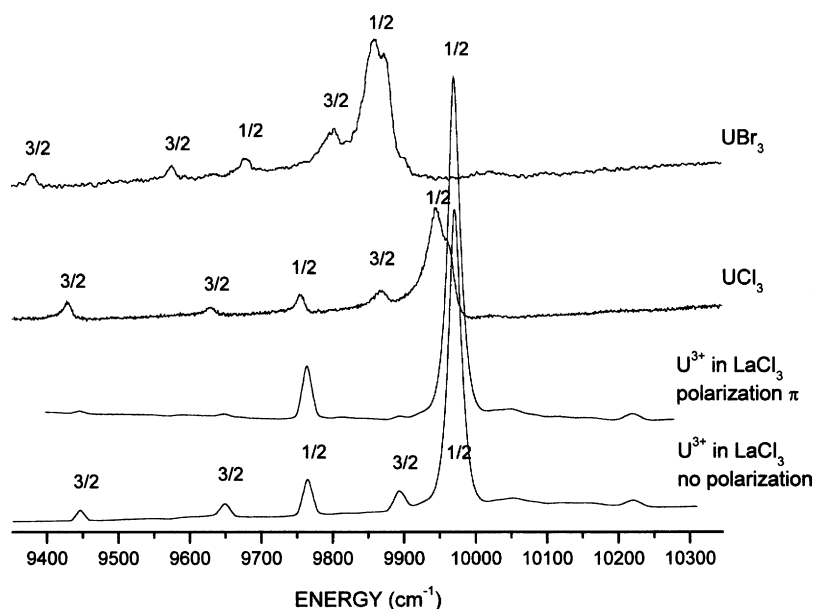


Fig. 3. A comparison of the UCl_3 and UBr_3 absorption spectra with those of $U^{3+} : LaCl_3$ single crystals [10] for the ${}^2H_{29/2}$ and ${}^4F_{5/2}$ multiplets.

ranges, respectively (Fig. 1). The recorded bands are relatively intense, sharp and well separated. One could also observe an expected red shift of these bands in the UBr_3 spectrum as well as of the first strong $5f^3 \rightarrow 5f^2 6d^1$ bands from about $22\,150\text{ cm}^{-1}$ for UCl_3 to $20\,150\text{ cm}^{-1}$ for UBr_3 (Figs. 1–3). Since above these wave numbers, the $5f^3 \rightarrow 5f^3$ transitions are obscured by strong and broad $5f^3 \rightarrow 5f^2 6d^1$ bands, the analysis has been limited to the above-mentioned absorption ranges. A comparison of the recorded $5f^3 \rightarrow 5f^3$ transitions with those determined for $\text{U}^{3+}:\text{LaCl}_3$ [10] (Fig. 3) enabled an unambiguous identification of 57 and 46 crystal-field bands for UCl_3 and UBr_3 , respectively. These experimental levels were then fitted to the parameters of the phenomenological Hamiltonian. As initial values of the free-ion and crystal-field parameters were taken, those determined for U^{3+} doped LaCl_3 single crystals [10].

Table 1

Hamiltonian parameters (in cm^{-1}) obtained from crystal-field (CF) and correlation crystal field (CCF) analyses of UCl_3 and $\text{U}^{3+}:\text{LaCl}_3$ [10]

Parameter ^a	CF (UCl_3)	CCF (UCl_3)	CCF ($\text{U}^{3+}:\text{LaCl}_3$ [10])
E_{avg}	19 331(42)	19 360(3)	19 426(34)
F^2	37 732(156)	38 311(10)	38 459(128)
F^4	30 350(203)	30 682(17)	30 786(161)
F^6	19 452(220)	19 349(17)	19 981(174)
α	32(6)	32(1)	31(4)
β	−939(40)	−948(7)	−886(34)
γ	2092(116)	2051(8)	1928(93)
ζ	1607(14)	1604(2)	1614(11)
T^2	456(82)	293(6)	388(68)
T^3	58(26)	53(6)	39(22)
T^4	160(39)	176(6)	154(33)
T^6	−145(46)	−212(8)	−233(38)
T^7	359(43)	389(9)	401(35)
T^8	[300]	[300]	[300]
M^j	[0.672]	[0.672]	[0.672]
P^k	1641(66)	1700(13)	1491(52)
B_0^2	369(42)	346(11)	312(33)
B_0^4	−362(77)	−387(19)	−459(66)
B_0^6	−1710(75)	−1576(18)	−1462(55)
B_6^6	936(61)	950(15)	1027(47)
$G_{10A,0}^4$		1470(32)	1001(98)
$G_{10B,0}^4$		460(27)	484(91)
$G_{2,0}^4$		657(53)	817(181)
$G_{10B,0}^6$		−1161(35)	−1590(108)
n	57	57	57
σ^b	36	31	29
N_V^c	2049.0	1945	1904

The M^j and P^k parameters were constrained by Hartree–Fock determined fixed values [2].

^aThe parameters are defined in Section 3. Values in brackets indicate parameter errors. Parameters in square brackets were kept constant during the fitting procedure.

^bstandard deviation: $\sigma = \sum_i [(\Delta_i)^2 / (n - p)]^{1/2}$ where Δ_i is the difference between the observed and calculated energies, n is the number of levels fitted, and p is the number of parameters freely varied.

^c N_V is the crystal field strength parameter (see Eq. (6)).

Table 2

Hamiltonian parameters (in cm^{-1}) obtained from crystal-field (CF) and correlation crystal field (CCF) analyses of UBr_3

Parameter ^a	CF	CCF
E_{avg}	19 236(75)	19 213(60)
F^2	38 097(269)	37 931(216)
F^4	31 225(316)	30 281(256)
F^6	21 232(318)	20 536(257)
α	27(8)	29(7)
β	−818(54)	−864(46)
γ	1576(170)	1690(136)
ζ	1605(19)	1606(16)
T^2	301(127)	347(105)
T^3	26(34)	17(28)
T^4	277(58)	252(48)
T^6	−285(80)	−303(64)
T^7	271(60)	292(50)
T^8	[300]	[300]
M^j	[0.672]	[0.672]
P^k	1697(89)	1616(76)
B_0^2	402(50)	350(43)
B_0^4	−459(86)	−562(78)
B_0^6	−1661(78)	−1568(69)
B_6^6	730(63)	770(54)
$G_{10A,0}^4$		969(135)
$G_{10B,0}^4$		744(103)
$G_{2,0}^4$		793(207)
$G_{10B,0}^6$		−1399(126)
n	46	46
σ^b	31	31
N_V^c	1970	1923

The M^j and P^k parameters were constrained by Hartree–Fock determined fixed values [2].

^aThe parameters are defined in Section 3. Values in brackets indicate parameter errors. Parameters in square brackets were kept constant during the fitting procedure.

^bstandard deviation: $\sigma = \sum_i [(\Delta_i)^2 / (n - p)]^{1/2}$ where Δ_i is the difference between the observed and calculated energies, n is the number of levels fitted and p is the number of parameters freely varied.

^c N_V is the crystal field strength parameter (see Eq. (6)).

The calculations were performed for the full $5f^3$ electronic configuration leading to a 364×364 energy matrix. In the final fitting procedure 14 atomic “free ion” parameters, 4 one-electron crystal-field parameter and 4 correlation crystal-field (CCF) parameters were freely varied. The T^8 and M^0 parameters were kept at constant values. The complete parameter sets of UCl_3 and UBr_3 , for both fits are presented in Tables 1 and 2, respectively. The corresponding experimental and calculated energy values of the crystal-field levels are given in Tables 3 and 4.

In the absorption spectra recorded at 300 K one may observe temperature dependent satellite bands centered from one of the crystal field lines at 207 and 402 cm^{-1} in the spectrum of UCl_3 and at 198 and 375 cm^{-1} in that of UBr_3 . These values fit very well with the calculated energies of the Stark components of the $^4I_{9/2}$ ground level (Tables 3 and 4).

Table 3
Electronic states, symmetry labels, experimental and calculated energy levels of UCl_3

Multiplet ^a	Irrep	Exp.	Energy (cm^{-1})						
			CF		CCF				
			Calc.	$E-C$	Calc.	$E-C$			
$^4I_{9/2}$	$E_{5/2}$	0	46	-46	31	-31			
	$E_{1/2}$	207 ^b	203	4	229	-22			
	$E_{3/2}$	—	253		248				
	$E_{5/2}$	—	462*		407				
	$E_{3/2}$	442 ^b	451*	-9	438	4			
$^4I_{11/2}$	$E_{3/2}$	4456	4444	12	4442	14			
	$E_{1/2}$	4514	4480	34	4487	27			
	$E_{5/2}$	—	4556		4535				
	$E_{1/2}$	4567	4565	2	4538	29			
	$E_{3/2}$	4582	4570	12	4571	11			
$^4F_{3/2}$	$E_{5/2}$	—	4619		4602				
	$E_{1/2}$	7064	7063	1	7069	-5			
	$E_{3/2}$	7096	7081	15	7080	16			
	$^4I_{13/2}$	$E_{1/2}$	8129	8121	8	8129	0		
		$E_{3/2}$	8220	8232	-12	8229	-9		
$E_{1/2}$		8240	8241	-1	8250	-10			
$E_{5/2}$		—	8293		8284				
$E_{1/2}$		—	8319		8324				
$^2H_{29/2}$	$E_{3/2}$	8381	8354	27	8356	25			
	$E_{5/2}$	—	8433		8423				
	$E_{5/2}$	—	9481		9325				
	$E_{3/2}$	9430	9501	-71	9449	-19			
	$E_{3/2}$	9630	9646*	-16	9651	-21			
$^4F_{5/2}$	$E_{1/2}$	9756	9645*	111	9702*	54			
	$E_{5/2}$	—	9774		9674*				
	$E_{5/2}$	—	9877*		9863				
	$E_{3/2}$	9869	9872	-3	9879	-10			
	$E_{1/2}$	9946	9925	21	9917	29			
$^4G_{5/2}+$	$E_{1/2}$	11 054	11 046	8	11 042	12			
	$^4S_{3/2}+$	$E_{1/2}$	—	11 140*		11 152*			
		$^4F_{7/2}+$	$E_{3/2}$	11 143	11 136*	7	11 148*	-5	
			$^4I_{15/2}+$	$E_{5/2}$	—	11 169		11 159	
				$E_{1/2}$	—	11 217		11 229	
$E_{3/2}$				11 235	11 235	0	11 235	0	
$E_{1/2}$	—			11 468		11 481*			
$E_{3/2}$	11 436	11 485*		-49	11 463*	-27			
$^4G_{7/2}$	$E_{5/2}$	—	11 479*		11 437*				
	$E_{5/2}$	—	11 553		11 539				
	$E_{1/2}$	11 560	11 561	-1	11 535	25			
	$E_{3/2}$	11 620	11 629	-9	11 629	-9			
	$E_{5/2}$	—	11 742*		11 715				
$^4F_{9/2}$	$E_{1/2}$	11 715	11 741*	-26	11 743	-28			
	$E_{3/2}$	11 880	11 871	9	11 865	15			
	$E_{3/2}$	11 930	11 944	-14	11 933	-3			
	$E_{5/2}$	—	12 068		12 047				
	$E_{5/2}$	—	13 237*		13 231*				
$^4G_{9/2}$	$E_{3/2}$	13 261	13 226*	35	13 230	31			
	$E_{5/2}$	—	13 290		13 284				
	$E_{1/2}$	13 294	13 366	-72	13 356	-62			
	$^4F_{7/2}$	$E_{5/2}$	—	14 604		14 536			
		$E_{1/2}$	14 637	14 635	2	14 641	-4		
$E_{5/2}$		—	14 698*		14 649				
$E_{3/2}$		14 666	14 681*	-15	14 665	1			
$E_{3/2}$		14 737	14 715	22	14 729	8			
$^2H_{11/2}$	$E_{3/2}$	15 378	15 356	21	15 328	50			
	$E_{1/2}$	—	15 297*		15 363*				

Table 3 (continued)

Multiplet ^a	Irrep	Exp.	Energy (cm^{-1})				
			CF		CCF		
			Calc.	$E-C$	Calc.	$E-C$	
$^4D_{3/2}$	$E_{1/2}$	15 416	15 415*	1	15 455*	-39	
	$E_{3/2}$	—	15 363*		15 328*		
	$E_{5/2}$	—	15 488		15 376*		
	$E_{5/2}$	—	15 592		15 484		
	$E_{1/2}$	15 765	15 786	-21	15 785	-20	
$^2K_{13/2}$	$E_{3/2}$	15 829	15 818	11	15 822	7	
	$E_{1/2}$	15 895	15 899	-4	15 885	10	
	$E_{5/2}$	—	16 037		15 980		
	$E_{5/2}$	—	16 104*		16 040		
	$E_{3/2}$	—	16 069*		16 041		
$^4D_{1/2}$	$E_{1/2}$	—	16 099*		16 104		
	$E_{3/2}$	—	16 188		16 162		
	$E_{1/2}$	16 170	16 167	3	16 197	-27	
	$E_{1/2}$	16 435	16 447	-12	16 417	18	
	$^4G_{9/2}+$	$E_{5/2}$	—	16 743		16 711	
$^2G_{17/2}$		$E_{3/2}$	—	16 761		16 762	
		$E_{3/2}$	16 823	16 816	7	16 815	8
		$E_{1/2}$	16 884	16 832	21	16 855	29
		$E_{5/2}$	—	16 895		16 863	
	$E_{3/2}$	16 925	16 960*	-35	16 931	-6	
$^4D_{5/2}$	$E_{1/2}$	16 967	16 959*	8	16 969	-2	
	$E_{5/2}$	—	17 017		17 005		
	$E_{5/2}$	—	17 102		17 039		
	$E_{5/2}$	—	17 399		17 421		
	$E_{3/2}$	17 456	17 462	-6	17 467	-11	
$^2L_{15/2}$	$E_{1/2}$	—	17 478		17 509		
	$E_{1/2}$	—	18 402		18 410		
	$E_{1/2}$	18 471	18 489*	-46	18 501	-30	
	$E_{3/2}$	18 510	18 517*	21	18 508	2	
	$E_{5/2}$	—	18 644*		18 625*		
$^4D_{3/2}$	$E_{3/2}$	18 630	18 627*	3	18 614	16	
	$E_{1/2}$	18 686	18 664	21	18 662	24	
	$E_{3/2}$	18 723	18 722	1	18 711	12	
	$E_{5/2}$	—	18 764		18 746		
	$E_{1/2}$	19 109	19 111	-2	19 110	-1	
$^2H_{11/2}$	$E_{3/2}$	19 170	19 122	47	19 130	40	
	$E_{1/2}$	19 688	19 735	-47	19 751	-63	
	$E_{3/2}$	—	19 753		19 737*		
	$E_{5/2}$	—	19 802*		19 755		
	$E_{5/2}$	—	19 803*		19 766		
$^2D_{15/2}$	$E_{3/2}$	—	19 790*		19 774		
	$E_{1/2}$	19 812	19 764*	48	19 788	24	
	$E_{1/2}$	20 142	20 190	-48	20 171	-29	
	$E_{3/2}$	20 257	20 230	27	20 245	12	
	$E_{5/2}$	—	20 314		20 294		
$^2G_{19/2}+$	$E_{5/2}$	—	21 133		21 146		
	$^2P_{1/2}$	$E_{1/2}$	21 166	21 195	-29	21 209	-43
		$E_{3/2}$	—	21 244		21 262	
		$E_{1/2}$	21 310	21 285	25	21 281	29
		$E_{3/2}$	—	21 339		21 369	
$E_{5/2}$		—	—		—		

* Asterisks indicate levels for which the order of the calculated values is reversed.

^a Nominal quantum numbers for the atomic state associated with the group.

^b Values determined from analysis of the temperature-dependent satellite lines.

Table 4
Electronic states, symmetry labels, experimental and calculated energy levels of UBr_3

Multiplet ^a	Irrep	Exp.	Energy (cm ⁻¹)			
			CF		CCF	
			Calc.	E-C	Calc.	E-C
⁴ I _{9/2}	<i>E</i> _{5/2}	0	26	-26	17	-17
	<i>E</i> _{1/2}	198 ^b	179	19	209	-11
	<i>E</i> _{3/2}		240		240	
	<i>E</i> _{5/2}		411*		364	
	<i>E</i> _{3/2}	375 ^b	401*	-26	396	-21
⁴ I _{11/2}	<i>E</i> _{3/2}	4434	4410	24	4409	25
	<i>E</i> _{1/2}	4480	4460	20	4469	11
	<i>E</i> _{5/2}		4520		4500	
	<i>E</i> _{1/2}	4520	4527	-7	4539	-19
	<i>E</i> _{3/2}	4551	4539	12	4539	12
⁴ F _{3/2}	<i>E</i> _{5/2}		4577		4561	
	<i>E</i> _{1/2}	6984	6979	5	6977	7
	<i>E</i> _{3/2}	7002	7001	1	6986	16
⁴ I _{13/2}	<i>E</i> _{1/2}	8108	8092	16	8092	16
	<i>E</i> _{3/2}	8188	8199	-11	8186	2
	<i>E</i> _{1/2}	8209	8207	2	8209	0
	<i>E</i> _{5/2}		8264		8246	
	<i>E</i> _{1/2}		8275		8281	
² H _{29/2}	<i>E</i> _{3/2}	8293	8305	-12	8301	-8
	<i>E</i> _{5/2}		8373		8358	
	<i>E</i> _{5/2}		9435		9287	
	<i>E</i> _{3/2}	9379	9454	-75	9398	-19
	<i>E</i> _{3/2}	9577	9585	-8	9580	-3
⁴ F _{5/2}	<i>E</i> _{1/2}	9680	9586	94	9645	35
	<i>E</i> _{5/2}		9710		9647	
	<i>E</i> _{5/2}		9822*		9811	
	<i>E</i> _{3/2}	9802	9812*	-10	9816	-14
	<i>E</i> _{1/2}	9862	9859	3	9857	5
⁴ G _{5/2} +	<i>E</i> _{1/2}		10996		10983	
⁴ S _{3/2} +	<i>E</i> _{1/2}	11050	11053	-3	11050	0
⁴ F _{7/2} +	<i>E</i> _{3/2}		11101		11094	
⁴ I _{15/2} +	<i>E</i> _{5/2}		11141		11119	
	<i>E</i> _{1/2}	11212	11189*	23	11184*	28
	<i>E</i> _{3/2}	11151	11153*	-2	11164*	-13
	<i>E</i> _{1/2}	11361	11389*	-28	11393	-32
	<i>E</i> _{3/2}	11408	11433*	-25	11417*	-9
	<i>E</i> _{5/2}		11420*		11393*	
	<i>E</i> _{5/2}		11479		11475	
	<i>E</i> _{1/2}	11520	11491	29	11490	30
	<i>E</i> _{3/2}	11573	11597	-24	11586	-13
	<i>E</i> _{5/2}		11711*		11668	
	<i>E</i> _{1/2}	11663	11622*	1	11649	14
	<i>E</i> _{3/2}		11793		11784	
	<i>E</i> _{3/2}		11849		11827	
	<i>E</i> _{5/2}		11971		11940	
	⁴ G _{7/2}	<i>E</i> _{5/2}		13186*		13184*
<i>E</i> _{3/2}		13178	13174*	4	13179*	1
<i>E</i> _{5/2}			13232		13227	
<i>E</i> _{1/2}		13330	13318	12	13310	20
<i>E</i> _{5/2}			14534		14479	
⁴ F _{9/2}	<i>E</i> _{1/2}	14565	14574	-9	14596*	-31
	<i>E</i> _{5/2}		14624*		14596*	

Table 4 (continued)

Multiplet ^a	Irrep	Exp.	Energy (cm ⁻¹)			
			CF		CCF	
			Calc.	E-C	Calc.	E-C
² H _{211/2}	<i>E</i> _{3/2}		14618*		14620	
	<i>E</i> _{3/2}		14648		14679	
	<i>E</i> _{3/2}		15304*		15240	
	<i>E</i> _{1/2}	15293	15269*	24	15292	1
	<i>E</i> _{1/2}	15343	15379*	-36	15381*	-39
⁴ D _{3/2}	<i>E</i> _{3/2}		15334*		15307*	
	<i>E</i> _{5/2}		15472		15352	
	<i>E</i> _{5/2}		15551		15433	
	<i>E</i> _{1/2}	15643	15631	12	15627	16
	<i>E</i> _{3/2}	15697	15696	1	15701	-4
² K _{13/2}	<i>E</i> _{1/2}	15773	15764	9	15747	26
	<i>E</i> _{5/2}		15889*		15839	
	<i>E</i> _{5/2}		15945*		15889	
	<i>E</i> _{3/2}	15912	15914*	-2	15907	5
	<i>E</i> _{1/2}		15932*		15963	
⁴ D _{1/2}	<i>E</i> _{3/2}		16035*		16012	
	<i>E</i> _{1/2}	16052	16027*	25	16057	-5
	<i>E</i> _{1/2}	16295	16294	1	16275	20
	<i>E</i> _{5/2}		16681*		16657	
	<i>E</i> _{3/2}		16677*		16688	
⁴ G _{9/2} +	<i>E</i> _{3/2}	16727	16750	-23	16752	-25
	<i>E</i> _{1/2}	16821	16786	35	16773	48
	<i>E</i> _{5/2}		16838		16827	
	<i>E</i> _{3/2}	16857	16890*	-33	16864	-7
	<i>E</i> _{1/2}		16883		16903	
⁴ D _{5/2}	<i>E</i> _{5/2}		16957		16944	
	<i>E</i> _{5/2}		17028		16970	
	<i>E</i> _{5/2}		17226		17235	
	<i>E</i> _{3/2}		17301		17279	
	<i>E</i> _{1/2}		17325		17334	
² L _{15/2}	<i>E</i> _{1/2}		18184		18207	
	<i>E</i> _{1/2}	18303	18310*	-7	18321*	-18
	<i>E</i> _{3/2}		18262*		18285*	
	<i>E</i> _{5/2}		18453*		18435*	
	<i>E</i> _{3/2}		18426*		18425*	
⁴ D _{3/2}	<i>E</i> _{1/2}	18448	18464*	-16	18443	5
	<i>E</i> _{3/2}	18507	18510*	-3	18500	7
	<i>E</i> _{5/2}		18547		18537	
	<i>E</i> _{1/2}	18883	18893	-10	18901	-18
	<i>E</i> _{3/2}		18902		18917	
² H _{111/2}	<i>E</i> _{1/2}	19495	19550	-55	19563	-68
	<i>E</i> _{3/2}		19582		19575	
	<i>E</i> _{5/2}		19622		19584	
	<i>E</i> _{5/2}		19633		19603	
	<i>E</i> _{3/2}		19616		19604	
	<i>E</i> _{1/2}	19674	19594*	80	19627	47

* Asterisks indicate levels for which the order of the calculated values is reversed.

^a Nominal quantum numbers for the atomic state associated with the group.

^b Values determined from analysis of the temperature-dependent

As could be expected the obtained atomic and crystal-field parameters for UCl_3 are close to those reported for $\text{U}^{3+}:\text{LaCl}_3$ single crystals [10] with the largest difference of ca. 19% for the T^3 parameter. Somewhat larger

differences exhibit the values obtained for UBr_3 (see Table 2). The σ standard deviations (see Tables 1 and 2) are also close to the value of 29 obtained for $\text{U}^{3+}:\text{LaCl}_3$. Similarly as for $\text{U}^{3+}:\text{LaCl}_3$ the largest $E_{\text{obs}}-E_{\text{calc}}$

differences equal to -71 and 111 cm^{-1} and also -75 and 94 cm^{-1} are observed for the corresponding levels of the $^2H_{9/2}$ multiplet at 9430 and 9756 cm^{-1} as well as 9379 and 9680 cm^{-1} for UCl_3 and UBr_3 , respectively (Tables 3 and 4). The inclusion of the CCF parameters enabled a decrease of these Δ values as well as of the standard r.m.s. deviation for the overall fitting (Tables 3 and 4).

Generally, one observes in the UCl_3 spectrum only somewhat larger crystal-field splittings of the $^{2S+1}L_J$ multiplets as compared with that of UBr_3 (Tables 3 and 4). The magnitude of the total crystal-field strength may be expressed by the scalar parameter [16]

$$N_v = \left[\sum_{k,q} (B_q^k)^2 \frac{4\pi}{(2k+1)} \right]^{1/2}. \quad (6)$$

The N_v values, calculated for the appropriate sets of parameters (see Tables 1 and 2) obtained with and without (values in parantheses) inclusion of the CCF parameters, are equal to 1945 (2049) and 1923 (1970) for UCl_3 and UBr_3 , respectively. The N_v value for UCl_3 is, as expected, somewhat larger than that for $U^{3+}:\text{LaCl}_3$, $N_v = 1904$ (1917) [10]. The obtained values correspond also with the dependence of N_v from the values of the total crystal-field splitting of the ground multiplet, reported in our previous studies for the so far investigated U^{3+} complex chlorides [6].

The relatively small differences between the values obtained for UCl_3 and UBr_3 may arise from comparable large crystal-field splittings (see Tables 3 and 4). Since the Hamiltonian parameters for $Nd^{3+}:\text{LaCl}_3$ [17] and $NdCl_3$ [18] have also been determined, we have calculate the ratios of their values for $U^{3+}:\text{LaCl}_3 / Nd^{3+}:\text{LaCl}_3$ and $UCl_3 / NdCl_3$ and have found that they are almost identical. The relatively small r.m.s. deviation as well as the good relationship between the computed crystal-field parameters for U^{3+} and Nd^{3+} allowed us to conclude that the obtained values are well determined.

5. Conclusions

The paper presents the first low-temperature electronic absorption spectra of polycrystalline samples of UCl_3 and UBr_3 as well as the first crystal-field energy level analyses for these two basic uranium(III) compounds. The analysis enabled the assignment of

most of the observed $5f^3 \rightarrow 5f^3$ transitions in the investigated absorption ranges and the determination of the crystal-field parameters. The inclusion of contributions from two electron correlation crystal-field interactions enabled the elimination of major discrepancies between the calculated and observed energy levels within the $^2H_{9/2}$ multiplet. The results are also in good agreement with those reported in earlier studies of other U^{3+} systems.

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