Spectrum analysis, correlation crystal-field effects and f-f transition intensities of U³⁺ in LaCl₃

M. Karbowiak, J. Drożdżyński,^{a)} and M. Sobczyk Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

(Received 16 January 2002; accepted 11 April 2002)

High resolution polarized absorption spectra of U^{3+} :LaCl₃ single crystals were recorded in the 4000–50 000 cm⁻¹ range at 7 K. The experimental crystal-field energy levels of the U^{3+} ion were fitted to a semiempirical Hamiltonian employing free-ion, one-electron crystal-field as well as two-particle correlation crystal-field (CCF) operators. The performed analysis of the spectra enabled the determination of crystal-field parameters and reassignment of some of the observed $5f^3 \rightarrow 5f^3$ transitions. The effects of selected CCF operators on the splitting of some specific U^{3+} multiplets have been investigated. On the basis of the obtained electronic wave functions the electric-dipole intensity parameters of the total transition dipole strength were determined by fitting the calculated and experimental transition intensities. Among 67 transitions observed in the 4000–22 000 cm⁻¹ range 56 were sufficiently well resolved for quantitative calculations. © 2002 American Institute of Physics. [DOI: 10.1063/1.1482372]

I. INTRODUCTION

The first crystal-field analysis of a U³⁺ system has been reported in 1980 by Crosswhite et al.¹ for U³⁺:LaCl₃ single crystals and subsequently revised by Carnall.² In recent years further analyses were reported for U^{3+} doped LiYF₄,³ RbY_2Cl_7 ,⁴ K₂UX₅ (X=Cl, Br or I),⁵ Cs₂NaYCl₆,⁶ and Cs_2LiYCl_6 (Ref. 6) single crystals as well as for some polycrystalline samples.^{7–9} However, from among the so far obtained U³⁺ doped single crystals only LaCl₃ and LiYF₄ exhibit a suitable site symmetry for precise energy-level structure investigations with application of electric and magnetic-dipole transition selection rules. In the latter one³ the uranium(3+) ions were obtained by γ irradiation of 700 to 1500 ppm U^{4+} doped single crystals. Since the recorded spectrum obviously contained additional lines of unknown origin, the crystal-field spectrum analysis may not be considered as unambiguous.

In this paper we have performed correlation crystal-field (CCF) calculations for U^{3+} doped LaCl₃ single crystals in order to use the obtained wave functions for simulation of transition intensities. So far such analyses have been reported for a number of lanthanide ions and the U^{3+} :LiYF₄ single crystal.¹⁰

Krämer *et al.*¹¹ have obtained an excellent agreement between the experimental and calculated line strengths for Er^{3+} doped LaCl₃ single crystals by utilizing the wave functions received from CCF calculations for simulation of f-f transitions intensities and have proved the correctness of this theoretical model for the lanthanide ions. The analysis reported by Hubert *et al.*¹⁰ for U³⁺ in LiYF₄ is limited to the 4540–11760 cm⁻¹ absorption range and therefore seems to be of not much significance. The aim of our study was to show how this model will work for an actinide ion. The experimental intensities were determined from lowtemperature σ and π -polarized absorption spectra. Since the transition intensities depend very strongly on the calculated wave functions they are a good test for the correctness of the crystal-field analysis, as well.

II. EXPERIMENT

Uranium(3+) doped single crystals of LaCl₃ with a nominal 0.5 and 0.1 mol% uranium concentration were grown in silica ampoules by the Bridgman–Stockbarger method. LaCl₃ was synthesized from the oxide by the ammonium chloride route and sublimed under high vacuum. UCl₃ was prepared according to the method reported in Ref. 12. Polarized absorption spectra of the LaCl₃:U³⁺ single crystals were recorded on a Cary 5 NIR-Vis-UV spectrophotometer in the 4000–50 000 cm⁻¹ range at 4.2 K using an Oxford Instruments cryostat. The crystal with inductively coupled plasma (ICP) determined uranium concentration of 0.0399 mol/dm³ and the thickness of 0.055 cm was used for quantitative measurements of oscillator strengths. The crystal was protected from moisture on air by a thin layer of nujol oil and in the Oxford Instruments cryostat by He gas.

III. METHODOLOGY

A. Optical selection rules

LaCl₃ crystallizes in the UCl₃-type structure (space group P6₃/m, No. 176) which consists of [MCl₉] polyhedra formed by trigonal prisms capped on each rectangular face.¹³ The uranium doped ions are occupying the La³⁺ position with the C_{3h} site symmetry. The crystal field splits the atomic states of the 5 f^3 configuration into Kramers doublets which may be classified as having the $E_{1/2}(\Gamma_7 + \Gamma_8)$, $E_{3/2}(\Gamma_{11} + \Gamma_{12})$ or $E_{5/2}(\Gamma_9 + \Gamma_{10})$ symmetry in the C_{3h} double-rotation group.

2800

^{a)}Author to whom correspondence should be addressed. Electronic mail: jd@wchuwr.chem.uni.wroc.pl



FIG. 1. Polarized absorption spectra of U^{3+} :LaCl₃ at 4.2 K showing the ${}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}$ transitions. The new and former^{1,2} (in brackets) assignments of observed lines are indicated. The inset gives selection rules for electric-dipole and magnetic-dipole transitions in U^{3+} :LaCl₃ (site symmetry C_{3h}). σ and π correspond to $E \perp c$ and $E \parallel c$, respectively.

The selection rules for electric-dipole and magneticdipole transitions are given in Fig. 1. The lowest crystal-field level of the ground ${}^{4}I_{9/2}$ multiplet manifold of U^{3+} has the $E_{5/2}$ symmetry. Since the transitions observed in liquid helium temperature originate only from this level they must terminate on the $E_{3/2}$ or $E_{1/2}$ excited level for σ polarization and $E_{1/2}$ for π polarization. Hence, the selection rules allow one an unambiguous assignment of the irrep labels of all lines observed in the spectrum.

B. Crystal-field energy calculations

Crystal-field calculations have been performed by applying the *f*-shell empirical program of Reid (University of Canterbury, New Zealand) and running on PC under the Linux Mandrake operating system. The effective operator model was used for the analysis of the obtained data.¹⁴ 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:

$$\hat{H} = \hat{H}_A + \hat{H}_{CF} + \hat{H}_{CCF},\tag{1}$$

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

$$\begin{split} \hat{H}_{A} &= E_{\text{ave}} + \sum_{k=0,2,4,6} F^{k}(nf,nf) \hat{f}_{k} + \zeta_{5f} \hat{A}_{\text{SO}} \\ &+ \alpha \hat{L}(\hat{L}+1) + \beta \hat{G}(G_{2}) + \gamma \hat{R}(R_{7}) \\ &+ \sum_{i=2,3,4,6,7,8} T^{i} \hat{t}_{i} + \sum_{j} M^{j} \hat{m}_{j} + \sum_{k} P^{k} \hat{p}_{k}, \end{split}$$
(2)

where E_{ave} is the spherically symmetric one-electron part of the Hamiltonian, $F^k(nf,nf)$ and ζ_{5f} represent the radial parts of the electrostatic and spin–orbit interactions, while f_k and A_{SO} are the angular parts of these interactions, respectively. The α , β , and γ parameters are associated with the two-body correction terms. $G(G_2)$ and $G(R_7)$ are Casimir operators for the G_2 and R_7 groups and L is the total orbital angular momentum. The three-particle configuration interaction is expressed by $T^i t_i$ (i=2,3,4,6,7,8), where T^i are parameters and 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 m_j and p_k , respectively. The \hat{H}_{CF} term of the Hamiltonian represents the one electron crystal-field interactions and is defined as

$$\hat{H}_{\rm CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i),$$
(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 expressed¹⁴ as follows:

$$H_{\rm CF} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_6^6 (C_{-6}^6 + C_6^6) + B_6'^6 i (C_{-6}^6 - C_6^6).$$
(4)

Depending on an arbitrary choice of the coordinate system the B_6^6 parameter can be either complex, purely real or purely imaginary. In the present analysis, the chosen coordinate system of the imaginary part of B_6^6 vanishes.

The last term of the complete Hamiltonian represents the correlated two-electron crystal-field interactions. Following Reid¹⁵ the parametrization of these interactions may be written in Judd's notation¹⁶ as a set of G_{iO}^{K} parameters:

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

Downloaded 07 Oct 2002 to 156.17.55.206. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

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

Since there are 41 independent correlation crystal-field (CCF) parameters it is not possible to include all of them in a fit with a set of 67 experimental data only. However, Li and Reid¹⁷ in an analysis of a number of Nd³⁺ doped crystals have shown that the inclusion of only a few of them have markedly improved the fits and could resolve problems with poorly fitted levels by the one-electron crystal-field operator H_{CF}. On the other hand, there arises the question which of the 41 parameters should be chosen. One possibility is to find those with the largest influence on the problematic levels. Although such a selection may be statistically justified, most probably it would have little physical meaning. Judd¹⁸ had invented the simple δ -function model in which the correlation effects are considered from paired electrons within the same angular f orbital only (with opposite spin). The validity of this model has been tested and proved by Quagliano et al.¹⁹ for neodymium nonahydrate tris(trifluoromethanesulfonate). Consequently, in the case of the $4f^3$ configuration only multiplets of a predominantly doublet character should be significantly influenced by two-electron correlationcrystal-field interactions. In the present analysis we have found the levels of the ${}^{2}H2_{9/2}$ multiplet to be the most problematic ones (see Sec. IV) and therefore we reduced the set of CCF parameters by applying the δ -function model restrictions.

The δ -function model are only contributing the $g_1^{(k)}$, $g_2^{(k)}$, $g_3^{(k)}$, and $g_4^{(k)}$ operators from among which the $g_1^{(k)}$ contribution is already incorporated in $H_{\rm CF}$. We have checked the effect of all these parameters and have proved that only the 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.

C. Transition line strengths

The experimental line strengths of transitions from the lowest Stark component of the ${}^{4}I_{9/2}$ ground multiplet to excited levels have been determined from the 7 K σ and π -polarized absorption spectra. The observed transition line profiles were integrated and the line strengths $S_{i \to f}$ in squared Debye units (D^2) $(D \equiv 3.3356 \times 10^{-30} \text{ C m})$ determined from the equation

$$S_{i \to f}(D^2) = \frac{9.186 \times 10^{-3}}{\chi_{\text{ed}} \tilde{\nu}} \int_{i \to f} \varepsilon(\tilde{\nu}) d\tilde{\nu}, \qquad (6)$$

where assuming a predominance of electric-dipole contribution to the transition intensities, the correction factor for bulk refractivity χ_{ed} is defined as

$$\chi_{\rm ed} = \frac{(n^2 + 2)^2}{9n},\tag{7}$$

and is for n = 1.849 equal to 1.7645.

Assuming, that the observed line strengths arise exclusively from electric- and magnetic-dipole transition mechanisms, the line strengths may be calculated by the evaluation of

$$S_{i \to f} = |\langle \psi_i | \hat{\mu}_{\text{eff}} | \psi_f \rangle|^2 + |\langle \psi_i | \hat{m} | \psi_f \rangle|^2, \qquad (8)$$

where $\hat{\mu}_{eff}$ is an effective electric-dipole operator, \hat{m}_{eff} is the magnetic-dipole operator, Ψ_i and Ψ_f are eigenvectors of the initial and final levels for the $i \rightarrow f$ transition. $\hat{\mu}_{eff}$ is defined as an even-parity operator that operates only within the $5f^3$ electronic configuration. The $\hat{\mu}_{eff}$ operator includes the combined perturbation of odd-parity crystal-field interactions and odd-parity electric-dipolar radiation field interactions on the 5f electrons of the system. The radial dependence of electric-dipole matrix elements is entirely absorbed in the parametric form of the $\hat{\mu}_{eff}$ operator. The qth component of the $\hat{\mu}_{eff}$ operator in a spherical basis representation is given by

$$(\hat{\mu}_{\rm eff})_q = -e(-1)^q \sum_{\lambda,t,p,l} A^{\lambda}_{t,p} \langle \lambda l, 1 - q | tp \rangle \hat{U}^{\lambda}_l, \qquad (9)$$

where $\lambda = 2,4,6$; $t = \lambda$, $\lambda \pm 1$; $p = 0, \pm 1, \pm 2, ..., \pm t$, and 1 = q + p. $\hat{U}_l^{(\lambda)}$ are interconfigurational many-electron unit tensor operators that act within the $5f^3$ electronic configuration, and A_{tp}^{λ} are parameters that contain structural and mechanistic details about the interaction of the odd-parity crystal-field and the electric-dipolar radiation field with the 5f electrons of the U^{3+} ion.

For the C_{3h} site symmetry the *p* values are restricted to ± 3 . The A_{tp}^{λ} parameters are related by the expression $(A_{t,p}^{\lambda})^* = (-1)^{t+p+l} A_{t,-p}^{\gamma}$. There are seven independent complex parameters: $A_{3,3}^2$, $A_{4,3}^4$, $A_{5,3}^4$, $A_{5,3}^6$, $A_{6,3}^6$, and $A_{7,3}^6$. In the line-strength calculations the $\langle \psi_i | \hat{U}_i^{(\lambda)} | \psi_f \rangle$ matrix elements were directly evaluated by using the Ψ_i and Ψ_f eigenfunctions obtained from the energy-level calculations. In the fitting procedure of the calculated and experimental line strengths the A_{tp}^{λ} parameters are treated as variables. The magnetic-dipole contributions were obtained from direct evaluation of the $\langle \Psi_i | \hat{m}_q | \Psi_f \rangle$ matrix elements. This contributions are considerable only for transitions to levels of the ${}^4I_{11/2}$ multiplet.

IV. RESULTS AND DISCUSSION

A. Energy level calculations

In his latest analysis² of the U^{3+} :LaCL₃ absorption spectrum, Carnall had included in the fitting procedure 82 experimental energy levels which could be recorded up to 25723 cm^{-1} . However above 22000 cm^{-1} the f-f bands are obscured by strong and broad f-d bands and also one cannot be fully sure as well about the origin and assignment of these sharp lines superimposed on the envelope of the f-d bands. Since the main purpose of our analysis was to obtain reliable eigenfunctions with a quality high enough for reproducing transition intensities, we have confined our analysis to the $0-22000 \text{ cm}^{-1}$ region, i.e., below the appearance of the f-d bands. Hence, from 7 K unpolarized as well as σ - and π -polarized absorption spectra we could isolate and assign 67 energy levels which were fitted to the parameters of the phenomenological Hamiltonian. The initial values of the free-ion and crystal-field parameters were taken from Carnall's analysis.² The calculations were done for the full $5f^3$ electron configuration leading to a 364×364 energy

Downloaded 07 Oct 2002 to 156.17.55.206. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE I. Hamiltonian parameters (in cm⁻¹) obtained from crystal-field (CF) and correlation crystal-field (CCF) analyses of U^{3+} :LaCl₃. The M^j and P^k parameters were constrained by Hartree–Fock determined fixed ratios.

Parameter ^a	CF	CCF
Eavg	19 418 (40)	19 426 (34)
$F^{2^{\circ}}$	38 269 (149)	38 459 (128)
F^4	30 530 (189)	30 786 (161)
F^6	19 770 (206)	19 981 (174)
α	31 (5)	31 (4)
β	- 886 (38)	- 886 (34)
γ	2059 (109)	1928 (93)
ζ	1612 (13)	1614 (11)
T^2	394 (78)	388 (68)
T^3	48 (24)	39 (22)
T^4	169 (37)	154 (33)
T^6	-192 (43)	-233(38)
T^7	358 (40)	401(35)
T^8	[300]	[300]
M^0	[0.672]	[0.672]
P^2	1579 (61)	1491 (52)
B_0^2	339 (39)	312 (33)
B_0^4	- 399 (71)	-459 (66)
B_{0}^{6}	-1549 (63)	-1462 (55)
B_{6}^{6}	934 (55)	1027 (47)
$G_{10A,0}^4$		1001 (98)
G_{10R0}^4		484 (91)
G_{20}^{4}		817 (181)
$G_{10B0}^{6^{2,0}}$		- 1590 (108)
$\sigma^{\rm b}$	34	29
n	67	67

^aThe parameters are defined in Sec. III B. 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.

matrix. In the final fitting procedure, 14 atomic parameters, four one-electron crystal-field parameters, and four CCF parameters were freely varied. The T^8 and M^j parameters were kept at constant value. The P^2 parameter was varied while P^4 and P^6 were kept at a constant ratio to P^2 . For comparison we have performed also a fit without the CCF parameters. The complete parameter sets for both fits are presented in Table I. The experimental and calculated energy level values are given in Table II. The atomic parameters are generally similar to those reported by Carnall. One may notice somewhat lower values of the F^k parameters and slightly larger for α and β . The largest difference exhibits the γ parameter with a factor almost of twice larger value than in the previous analysis. However, this parameter was usually set at a constant value of ca. $1000-1100 \text{ cm}^{-1}$. As compared with Nd^{3+} ions²⁰ the α and β parameters display somewhat larger values. The γ parameter for Nd³⁺ is usually about 1500 cm^{-1} . Hence, the value of about 2000 cm^{-1} obtained in this analysis seems to be reasonable. The three-body T^{i} parameters assumed in our fit are also similar values to those reported earlier. In the application of the one-electron parametrization scheme we could receive the standard deviation of $\sigma = 34.0 \text{ cm}^{-1}$. The B_q^k parameters obtained in this fit were close to those reported by Carnall except of B_0^4 , which in our fit has a distinctly different value (-399 cm⁻¹) as compared to the former one (-662 cm⁻¹).

From Table II one can note, that for some levels the $E_{\rm calc} - E_{\rm obs}$ differences are significantly larger. The largest differences can be observed for these recorded at 9446 and 9764 cm⁻¹ levels of the ${}^{2}H2_{9/2}$ multiplet for which these values are equal to -83 and 101 cm^{-1} , respectively. Even the order of the calculated values was reverse. The overall splitting of this multiplet was underestimated by more than 100 cm^{-1} in the one-electron calculation model. After inclusion of the CCF parameters the order became correct and the Δ values decreased to 30 and 34 cm⁻¹, respectively. The standard rms deviation for the overall fitting decreased to 28.9 cm^{-1} . In the two-electron parametrization scheme the values of the B_a^k parameters did not change markedly as compared to those obtained without CCF parameters but the obtained values were then somewhat closer to those reported by Carnall. This was due to the fact, that the influence of inclusion of problematic crystal-field levels in the fit without CCF parameters was then absorbed by these parameters.

The values of the fourth-rank CCF parameters are relatively high, e.g., $G_{10A,0}^4$ is more than a factor of 2 larger than B_0^4 , and $G_{10B,0}^6$ is of the same order as B_0^6 . Since the $\hat{g}_i^{(K)}$ operators are normalized differently for i = 1 and i > 1 one must multiply the B_q^k parameters by¹⁵ 14×(12/17)^{1/2} for a comparison. The renormalized "true" $G_{10A,0}^4/B_0^4$ and $G_{10B,0}^6/B_0^6$ ratios are then equal to -0.39 and -0.20, respectively. For the Nd³⁺ ions the average corrected $G_{10A,0}^4/B_0^4$ ratio is about 17 – 0.1. This may indicate stronger correlation effects of the $5f^3$ electrons as compared with $4f^3$. However, the diagonal "free-ion" reduced matrix elements of the $\hat{g}_{10A}^{(4)}$ operator for the ${}^{2}H2_{9/2}$ and ${}^{2}H2_{11/2}$ multiplets of the U³⁺ ion (obtained after taking into account the Coulomb and spinorbit interactions) are equal to 0.334 and 0.336, respectively, and are somewhat lower in comparison with 0.427 and 0.518 obtained for the analogous multiplets of the Nd³⁺ ion. Thus, the relatively larger $G_{104,0}^4/B_0^4$ ratio obtained for U³⁺ may simply result from stronger crystal-field interactions experienced by the U^{3+} ions. It is also possible that the observed improvement in the adjustment of some levels as well as a slightly better overall fit have nothing to do with the correlation effect but they result from the deficiency of the applied theoretical model for description of the crystal-field energy levels for the $5f^3$ configuration.

As has been mentioned above we are not sure about the origin of lines superimposed on the broad f-d bands observed over 22 000 cm⁻¹. If one assumes that these are f-f bands one should expect, that the distinct lines at 23 888 and 24 123 cm⁻¹ should belong to the ${}^{2}I_{13/2}$ multiplet. However, the inclusion of these levels in the calculations shows that the lowest crystal-field level of this multiplet was calculated to be at 24 377 cm⁻¹ giving a ΔE difference of about 400 cm⁻¹. Those levels have been omitted in Carnall's analysis. Other experimental levels observed in this region generally fit with the calculated ones. However, for more than 45 levels predicted by theory in this region we could register not more than 17. Hence, the assignment would be

TABLE II. Electronic states, symmetry labels, experimental and calculated energy levels, and line strengths of U^{3+} :LaCl₃.

		Energy (cm ⁻¹)					Line strength $(10^{-6} \text{ D}^2)^a$			
		CF			CCF		σ		π	
Mutliplet	Irrep.	Expt.	Calc. ^b	E-C	Calc.	E-C	Calc.	Obs.	Calc.	Obs.
${}^{4}I_{9/2}$	E 5/2	0	47	-47	39	- 39				
	$E_{1/2}$	208	202	6	238	-30	3876		360	
	$E_{3/2}$	245	239	6	236	9	486		231	
	$E_{5/2}$	440	437	3	403	36	397		210	
	$E_{3/2}$	451	432	19	437	13	358		6	
${}^{4}I_{11/2}$	$E_{3/2}$	4446	4442	4	4446	0	760	171	131	392
	$E_{1/2}$	4508	4478	30	4486	22	22 127	7130	872	3553
	E 5/2	4534	4540	-6	4527	7	124		8	
	$E_{1/2}$	4564	4559	5	4575	-11	907	1823	13 290	2100
	$E_{3/2}$	4580	4563	17	4569	11	791		2	
4	E 5/2	4610	4605	5	4598	12	0.6		0	
${}^{4}F_{3/2}$	$E_{1/2}$	7081	7082	-1	7083	-3	5360	(256)	2296	531
	$E_{3/2}$	7099	7099	0	7090	9	775	646	0	
${}^{4}I_{13/2}$	$E_{1/2}$	8133	8128	5	8128	5	20 927	(1617)	12 413	(1331)
	$E_{3/2}$	8221	8228	-7	8219	2	28		0	
	$E_{1/2}$	8242	8247	-5	8253	-11	7799	6368	13 198	7499
	E 5/2		8258		8271		0		0	
	$E_{1/2}$	8291	8319	-28	8328	-37	65		4912	
	$E_{3/2}$	8381	8350	31	8355	26	66	215	0	
2	E 5/2		8422		8418		0		0	
$^{2}H2_{9/2}$	E 5/2		9510		9368		0		0	
	$E_{3/2}$	9446	9529	-83	9476	-30	314	222	0	
	$E_{3/2}$	9648	9670*	-22	9671	-23	711	369	0	
	$E_{1/2}$	9764	9663*	101	9730	34	92	247	701	692
	E 5/2		9789		9751		7		1	
${}^{4}F_{5/2}$	E 5/2		9888*		9879		0		0	
	$E_{3/2}$	9889	9885*	4	9897	-8	913	831	0	
	$E_{1/2}$	9969	9938	31	9941	28	47 762	7222	11 098	8260
${}^{4}G_{5/2} +$	$E_{1/2}$	11 083	11 084	-1	11 076	6	4245	1753	11 352	2745
${}^{4}S_{3/2} +$	$E_{1/2}$		11 160		11 156		12 342		10 662	
${}^{4}F_{7/2} +$	$E_{3/2}$	11 174	11 174	0	11 170	4	7545		0	
${}^{4}I_{15/2} +$	E 5/2		11 199		11 188		0		0	
	$E_{1/2}$		11 234		11 216		1603		15 598	
	$E_{3/2}$	11 247	11 238	9	11 238	9	5307		0	
	$E_{1/2}$	11 437	11 484	-47	11 483*	-46	359		244	
	$E_{3/2}$	11 467	11 494	-27	11 464*	3	6945		0	
	$E_{5/2}$		11 499		11 471		0		0	
	$E_{5/2}$		11 570		11 557		0		0	
	$E_{1/2}$	11 575	11 574	1	11 579	-4	168		5722	
	$E_{3/2}$	11 620	11 630	-10	11 621	-1	757		0	
	E 5/2		11 725		11 681		0		0	
	$E_{1/2}$	11 727	11 748	-21	11 745	-18	272		1089	
	$E_{3/2}$	11 890	11 865	25	11 862	28	27		0	
	$E_{3/2}$	11 941	11 934	7	11 926	15	136		0	
4	E 5/2		12 051		12 034		0		0	
${}^{4}G_{7/2}$	E 5/2	13 233	13 268*	-35	13 260	-28	0		0	
	$E_{3/2}$	13 294	13 265*	29	13 271	23	6553	3096	0	
	E 5/2	13 320	13 326	-6	13 324	-4	0		0	
	$E_{1/2}$	13 344	13 394	-50	13 387	-43	11 814	6668	1248	7706
${}^{4}F_{9/2}$	E 5/2		14 636		14 585		0		0	
	$E_{1/2}$	14 675	14 669	6	14 684	-9	515	178	999	(103)
	E 5/2		14 722*		14 697		0		0	
	$E_{3/2}$	14 701	14 708*	-7	14 707	-6	90	78	0	
2	$E_{3/2}$		14 745		14 772		7		0	
$^{2}H2_{11/2}$	$E_{3/2}$	15 415	15 423*	-8	15 382	33	228	141	0	
	$E_{1/2}$	15 422	15 365*	57	15 395	27	1456	692	466	1107
	$E_{1/2}$	15 457	15 476*	-19	15 497*	-40	489	438	2649	784
	$E_{3/2}$	15 462	15 435*	27	15 427*	35	72	92	0	
	$E_{5/2}$		15 536		15 431*		0		0	
	$E_{5/2}$		15 641		15 541		0		0	
${}^{4}D_{3/2}$	$E_{1/2}$	15 825	15 853	-28	15 853	-28	3253	4799	2077	4999
	$E_{3/2}$	15 881	15 875	6	15 880	1	214	102	0	
$^{2}K_{13/2}$	$E_{1/2}$	15 961	15 970	-9	15 955	5	934	4176	4730	3323

TABLE II.	(Continued.)
-----------	--------------

		Energy (cm ⁻¹)				Line strength $(10^{-6} \text{ D}^2)^a$				
			CF		CCF		σ		π	
Mutliplet	Irrep.	Expt.	Calc. ^b	E-C	Calc.	E-C	Calc.	Obs.	Calc.	Obs.
	E 5/2		16 086		16 033		0		0	
	$E_{5/2}$		16 115		16 096		0		0	
	$E_{3/2}$		16 145		16 100		148		0	
	$E_{1/2}$		16 153		16 177		1517		104	
	$E_{3/2}$		16 231		16 224		44		0	
	$E_{1/2}$	16 231	16 225	6	16 268	-37	2953	5300	3170	7450
${}^{4}D_{1/2}$	$E_{1/2}$	16 507	16 523	-16	16 518	-11	1607		6218	
${}^{4}G_{9/2}^{1/2} +$	$E_{5/2}^{1/2}$		16 803		16 518		0		0	
${}^{2}G1_{7/2}$	$E_{3/2}^{3/2}$	16 863	16 825	38	16 822	40	98	122	0	
- 112	E 2/2	16 893	16 864	29	16 867	25	240	392	0	
	E1/2	16 930	16 908	22	16 888	42	994	2044	327	(2952)
	$E_{5/2}$		16 940		16 919		0		0	(_/ + _)
	$E_{2/2}$	16 947	16 999*	- 52	16 980	- 33	275		0	
	E 1/2	16 974	16 996*	-22	17 017	-43	699		312	
	E 1/2	10 // 1	17 051		17 044	10	0		0	
	E 5/2		17 137		17 097		0		0	
^{4}D	E 5/2		17/01		17 515		0		0	
$D_{5/2}$	E 5/2	17 536	17 538	-2	17 545	_ 0	976	1477	0	
	E 3/2	17 550	17 564	2	17 588	,	663	14//	2833	
2 ₁	E 1/2	18 514	18/186	25	18/195	10	445		120	
L 15/2	E 1/2	18 558	18 503*	- 35	18 580	- 22	1241	2445	2503	3800
	E 1/2	18 583	18 560*	14	18 581	22	1241	2054	2393	3077
	E 3/2	10 303	18 704*	14	18 674	2	0	2054	0	
	E 5/2	19 699	10 /04	0	18 677	11	204		0	
	E 3/2	10 000	10 000	11	10 0//	20	152		1777	
	E 1/2	10 745	10 705	20	10/15	50 17	435		1///	
	E 3/2	18 / 30	10/03	- 29	10 //3	-1/	155		0	
40	E 5/2	10 202	18 825	21	18 812	10	1014	2746	1017	4015
$D_{3/2}$	E 1/2	19 203	19 182	21	19 191	12	1814	2740	1917	4915
2 771	E 3/2	10 752	19 196	20	19 215	26	161	077	0	02
$^{2}H1_{11/2}$	E 1/2	19 /53	19 782	-29	19 7 / 9	-26	282	211	189	83
	E 3/2		19 801		19 /84		169		0	
	E 5/2		19 842		19 790		0		0	
	E 5/2		19 847		19 804		0		0	
	$E_{3/2}$		19 833		19 811		77		0	
2	$E_{1/2}$	19 875	19 812	63	19 835	40	600	577	1218	1361
$^{2}D1_{5/2}$	$E_{1/2}$	20 204	20 242	-38	20 230	-26	279	129	22	30
	$E_{3/2}$	20 3 10	20 282	28	20 286	24	21	161	0	
2	$E_{5/2}$		20 358		20 335		0		0	
${}^{2}G1_{9/2}+$	$E_{5/2}$		21 239		21 220		0	, .	0	
$^{2}P_{1/2}$	$E_{1/2}$	21 294	21 316	-22	21 309	-15	77	(629)	1384	1338
	$E_{3/2}$		21 337		21 348		22		0	
	$E_{1/2}$	21 400	21 378	22	21 394	6	396	(4748)	1555	1069
	$E_{3/2}$		21 424		21 437		89		0	
	E 5/2		21 487		21 485		0		0	

^aCalculated on the basis of eigenvalues resulted from CCF analysis.

^bCalculated Stark components denoted by an asterisk have been reordered to correspond to the experimental assignment.

very unrestricted and finally we did not include these levels in our calculations.

As compared with the other U^{3+} systems the received final rms deviation is somewhat larger which may result from a lesser discretion in the assignment of the experimental crystal-field levels, because in systems with a low site symmetry of the central ion they cannot be classified by irrep and therefore may be, to a certain degree arbitrary assigned within a multiplet to the closest calculated one.

The crystal field is somewhat weaker due to the comparatively long La–Cl distances which causes that the particular multiplets are relatively well separated and, except for two, they do not overlap. The correctness of the obtained crystal-field values may be checked also by calculations of the total crystal-field strength, expressed by the scalar parameter²¹

$$N_{v} = \left[\sum_{k,q} (B_{q}^{k})^{2} \frac{4\pi}{(2k+1)}\right]^{1/2}.$$
(10)

The calculated N_v value for U³⁺:LaCl₃ is 1891 cm⁻¹ (largest total splitting value $\Delta = 451$ cm⁻¹) and is expected to be larger than that determined for Nd³⁺:LaCl₃ (N_v = 1070 cm⁻¹, $\Delta = 241$ cm⁻¹) (Ref. 20) and somewhat

smaller than those for UCl₃ (N_v=2042 cm⁻¹, Δ =457 cm⁻¹ calc).²² These values correspond also with those reported in our previous spectroscopic studies on uranium(3+) complex chlorides: U³⁺:K₂LaCl₅ (N_v=3069 cm⁻¹, Δ =475 cm⁻¹),⁵ U³⁺:RbY₂Cl₇ (N_v=4354 cm⁻¹, Δ =567 cm⁻¹),⁴ U³⁺:Li₂NaYCl₆ (N_v=5496 cm⁻¹, Δ =595 cm⁻¹),⁶ and U³⁺:Cs₂NaYCl₆ (N_v=5816 cm⁻¹, Δ =626 cm⁻¹).⁶

The determined energy and symmetry labels of the levels are generally in agreement with those reported by Carnall, however we have found that some of them are inconsistent with selection rules for f-f transitions and should be reassigned.

In Fig. 1 the absorption spectrum in the ${}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}$ transition region is presented. Carnall's assignment is shown in brackets and the new one is indicated above. The very intense line observed at 8244 cm⁻¹ is undoubtedly $\sigma\pi$ polarized and one may label it as $E_{1/2}$ only. The lines at 8335 and 8358 cm⁻¹ were assigned by Carnall as electronic transitions. However, these lines are observed in π polarization but disappear in σ polarization, which is completely opposite to the selection rules because electric dipole transitions may not be observed in π polarization only. Hence those bands are in our analysis labeled as vibronic. At 8159 and 8267 cm⁻¹ two lines are observed with similar intensities.

TABLE III. $A_{t,p}^{\lambda}$ intensity parameter values (in units 10^{-12} cm^{-1}) of U^{3+} : LaCl₃. based on correlation crystal-field wave functions. The real part of $A_{4,3}^4$ and imaginary of $A_{5,3}^4$ are not statistically significant and have been set to zero.

Parameter	
A_{33}^2	-937 - 1387i (104 + 129 <i>i</i>)
$A_{3,3}^{4,5}$	1372 - 1298i (106 + 104i)
$A_{4,3}^{4,-}$	-1842i (90 <i>i</i>)
$A_{5,3}^{4}$	- 584 (83)
$A_{5,3}^{6}$	-608+848i (132+94 <i>i</i>)
$A_{6,3}^{6}$	952+2479 <i>i</i> (91+123 <i>i</i>)
$A_{7,3}^{6}$	1862+326 <i>i</i> (113+94 <i>i</i>)
N^{a}	56
$\sigma^{ m b}$	0.45

^aNumber of experimental transition line strengths used in the calculation. ^bDimensionless standard deviation defined according to Eq. (11).

The latter one has been included in Carnall's analysis and labeled as $E_{1/2}$, whereas the former one has been omitted. Since they are at the same distance of 24 cm⁻¹ from a neighboring strong line we assume that both of them are vibronic in origin.

The next change concerns a relatively strong line ob-



FIG. 2. Experimental (4.2 K) and calculated (dotted line) polarized absorption spectra of U^{3+} :LaCl₃ in the ${}^{4}I_{9/2} \rightarrow ({}^{2}H_{9/2} + {}^{4}F_{5/2})$ transition range. The figure presents one of the best fits from among the analyzed multiplets. A Gaussian line shape with the full width at half maximum corresponding to that of the appropriate experimental line has been used.

served at 9763 cm⁻¹ and assigned by Carnall as a magneticdipole transition. Since for transitions to the ${}^{2}H_{9/2}$ multiplet the magnetic-dipole contribution to their intensities is negligibly small and the line is clearly observed in σ and π polarization we have assigned it as an $E_{1/2}$ electric dipole transition.

The final change concerns two lines observed at 20 204 and 20 310 cm⁻¹ which have been omitted or assigned as vibronic in Carnall's analysis. Since they are too far away from the preceding lines of the ${}^{2}H_{11/2}$ multiplet they cannot be vibronic in origin. Hence, we have assigned them as components of the ${}^{2}D_{5/2}$ multiplet. As compared with Carnnall's calculations the position of this multiplet is now shifted by about 100 cm⁻¹.

B. Line strengths

Among transitions observed in the polarized absorption spectra only 35 in σ and 21 in π polarization were sufficiently well resolved to permit quantitative line strength deaccording to termination, Eq. (6).In the $11\,000-12\,100\,\mathrm{cm}^{-1}$ absorption range a number of levels originating from four multiplets overlap and we have not been able to determine reliable experimental line strengths in this region. From the intensity calculations it results, that magnetic-dipole transitions contribute markedly to the ${}^{4}I_{9/2}$ \rightarrow ⁴ $I_{11/2}$ transitions only. Since no lines of pure magneticdipole transitions $(E_{5/2} \rightarrow E_{5/2})$ were observed in the spectra the intensity calculations were performed for the electricdipole transitions only. The 56 experimental line strengths were fitted by the effective electric-dipole $A_{t,p}^{\lambda}$ parameters using the differential least-squares method. In the fitting procedure the quantity $[(I_{obs}-I_{calc})/(I_{obs}+I_{calc})]^2$ was minimized, where $I_{\rm obs}$ and $I_{\rm calc}$ are the observed and calculated line strengths, respectively. The quality of the fit is described by the dimensionless standard deviation defined as

$$\sigma = \left[\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{I_{\text{obs}} - I_{\text{calc}}}{I_{\text{obs}} + I_{\text{calc}}}\right)^2\right]^{1/2},\tag{11}$$

where n is a number of experimental data points and p is the number of freely varied parameters. For the C_{3h} site symmetry one has to determine seven complex $A_{t,p}^{\lambda}$ parameters for which the real and imaginary parts should be independently varied. However, the real part of $A_{4,3}^4$ and imaginary one of $A_{5,3}^4$ have proved to be statistically insignificant and have been set at zero which reduced the number of variables to 12. The obtained $A_{t,p}^{\lambda}$ parameters are listed in Table III. The uncertainties of the individual parameter values are expressed by the square roots of the respective diagonal elements of the error matrix multiplied by σ . The final standard deviation of the fit amounts to $\sigma = 0.45$, which corresponds to the uncertainty factor of $(1+\sigma)/(1-\sigma)=2.6$. Lines in parentheses, shown in Table III were not included in the intensity fit due to the large discrepancies between observed and calculated values.

The observed line strengths are one or two order of magnitude stronger as compared with those of Nd^{3+} in $[Nd(H_2O)_9](CF_3SO_3)_3$ (C_{3h} site symmetry)¹⁹ and about three orders of magnitude stronger as compared with Er^{3+}



FIG. 3. Experimental (4.2 K) and calculated (dotted line) polarized absorption spectra of U^{3+} :LaCl₃ in the ${}^{4}I_{9/2} \rightarrow {}^{4}I_{11/2}$ transition range. The figure presents one of the poorest fits from among the analyzed multiplets. A Gaussian line shape with the full width at half maximum corresponding to that of the appropriate experimental line has been used.

ions in LaCl₃.¹¹ In accordance with this the $A_{t,p}^{\lambda}$ parameters for U³⁺ are larger by one or two orders of magnitude, too.

As one could expect the obtained intensity simulation is not as good as for lanthanide ions. However, even if the absolute values for most multiplets are not very close to the experimental ones, the relative intensities of lines within a multiplet are quite well described. Figures 2 and 3 graphically present the results of one of the best fits for a multiplet and those where the quality of the simulation is rather poor. We have used a Gaussian line shape with the full width at half maximum corresponding to that of the appropriate experimental line. Since the energies of the lines were taken from our crystal-field calculation the figures allow one to compare the correctness of the energy levels simulation, too.

This is the first comprehensive intensity simulation attempt for U^{3+} ions. So far only Simoni *et al.*¹⁰ have performed a similar analysis for U^{3+} :LiYF₄ single crystals but due to difficulties in measuring of experimental intensities, resulting among others, from a low U^{3+} concentration, a stronger crystal field and an overlapping of multiplets, they could include in the fit only 19 band intensities centered in the 4540–11760 cm⁻¹ region, obtaining a standard deviation of 0.3.

As compared with intensity calculations performed for lanthanide ions, the obtained results are evidently worse, e.g., for Nd³⁺ in [Nd(H₂O)₉](CF₃SO₃)₃ where the Nd³⁺ ions are occupying the same site symmetry (C_{3h}) as U³⁺ in LaCl₃ the fit resulted in an error of 0.351.¹⁹ For 47 experimental levels of Er³⁺:LaCl₃ a very good agreement between experimental and calculated values with σ =0.2 has been also reported.¹¹ The presented studies however can serve as a good example of difficulties encountered in analysis of uranium ions as compared to those of lanthanides.

V. CONCLUDING REMARKS

The paper presents the most complete crystal-field energy level and line-strength analyses for any uranium(III) system. The crystal-field analysis of polarized low temperature absorption spectra enabled a reassignment of some of the observed $5f^3 \rightarrow 5f^3$ transitions. Including contributions from two-electron correlation crystal-field interactions, we could eliminate major discrepancies between the calculated and observed energy levels within the ${}^2H2_{9/2}$ multiplet.

The present study provides also a detailed analysis of line intensities associated with transitions between individual Stark levels. The calculations show that the applied model gives not as good results as it does for lanthanide ions.

ACKNOWLEDGMENT

This work was supported by the Polish Committee for Scientific Research within the Project No. 3 TO9A 090 10, which is gratefully acknowledged.

- ¹H. M. Crosswhite, H. Crosswhite, W. T. Carnall, and A. P. Paszek, J. Chem. Phys. **72**, 5103 (1980).
- ²W. T. Carnall, ANL Report 89/39.
- ³E. Simoni, M. Louis, J. Y. Gesland, and S. Hubert, J. Lumin. **65**, 153 (1995).
- ⁴ M. Karbowiak, J. Drożdżyński, K. M. Murdoch, N. M. Edelstein, and S. Hubert, J. Chem. Phys. **106**, 3067 (1997).
- ⁵M. Karbowiak, N. Edelstein, Z. Gajek, and J. Drożdżyński, Spectrochim. Acta, Part A 54, 2035 (1998).
- ⁶M. Karbowiak, J. Drożdżyński, S. Hubert, E. Simoni, and W. Stręk, J. Chem. Phys. **108**, 10181 (1998).
- ⁷M. Karbowiak and J. Drożdżyński, J. Alloys Compd. **300–301**, 329–333 (2000).
- ⁸M. Karbowiak, Z. Gajek, and J. Drożdżyński, Chem. Phys. **261**, 301 (2000).
- ⁹M. Karbowiak, J. Drożdżyński, and Z. Gajek, J. Alloys Compd. **323–324**, 678 (2001).
- ¹⁰E. Simoni, M. Louis, S. Hubert, and M. F. Reid, J. Phys. II 5, 755 (1995).
- ¹¹K. W. Krämer, H. U. Güdel, and R. N. Schwartz, Phys. Rev. B 56, 13830 (1997).
- ¹²J. Drożdzyński, Polyhedron 7, 167 (1988).
- ¹³T. Schleid, G. Meyer, and L. R. Morss, J. Less-Common Met. **132**, 69 (1987).
- ¹⁴B. G. Wybourne, Spectroscopic Properties of Rare Earths (Interscience, New York, 1965).
- ¹⁵M. F. Reid, J. Chem. Phys. 87, 2875 (1987).
- ¹⁶B. R. Judd, J. Chem. Phys. 66, 3163 (1977).
- ¹⁷C. L. Li and M. F. Reid, Phys. Rev. B 42, 1903 (1990).
- ¹⁸B. R. Judd, in *Lecture Notes in Physics*, edited by P. Kramer and A. Rieckers (Springer, Berlin, 1978), p. 417
- ¹⁹J. R. Quagliano, G. W. Burdick, D. P. Glover-Fischer, and F. S. Richardson, Chem. Phys. **201**, 321 (1995).
- ²⁰E. Rukmini, C. K. Jayasankar, and M. F. Reid, J. Phys.: Condens. Matter 6, 5919 (1994).
- ²¹F. Auzel and O. L. Malta, J. Phys. (Paris) 44, 201 (1983).
- ²²M. Karbowiak, J. Drożdzyński, and M. Sobczyk (unpublished).