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Parametric analysis of the energy levels of U^{4+} in D_{2d} and limiting D_2 sites in incommensurate $ThBr_4$

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Below $T_c = 95$ K, U^{4+}:$ThBr_4$ exists as an incommensurately modulated structure. The U^{4+} ions occupy a range of sites which vary from D_{2d} to a limiting D_2 site. The D_{2d} and limiting D_2 sites have been identifed spectroscopically. We report a parametric analysis of the U^{4+} energy levels in both sites. For 26 levels in the D_{2d} site the root-mean-square deviation $\sigma = 36$ cm^{-1} and $F^2 = 42\,253 \pm 127$, $F^4 = 40\,458 \pm 489$, $F^6 = 25\,881 \pm 383$, $\zeta = 1783 \pm 7$, $\alpha = 31 \pm 1$, $\beta = -644 \pm 75$, $\gamma = 1200$, $B_0^2 = -1096 \pm 80$, $B_0^4 = 1316 \pm 146$, $B_4^4 = -2230 \pm 85$, $B_0^6 = -3170 \pm 379$, and $B_4^6 = 686 \pm 246$, all in cm^{-1}. For 38 D_2 levels $\sigma = 39$ cm^{-1}, and those parameters which occur in both symmetries are only slightly changed. The additional parameters which occur only in D_2 symmetry are $B_2^2 = -78 \pm 30$, $B_2^4 = 318 \pm 122$, $B_2^6 = 136 \pm 101$, $B_6^6 = 123 \pm 125$, all in cm^{-1}. F^2 is 81% of the free-ion value. This decrease in F^2 is more like that found for $3d$ than that found for $4f$ electrons.

INTRODUCTION

The spectra of single crystals of U^{4+}:$ThBr_4$ and a preliminary analysis of the energy levels in D_{2d} site symmetry were published several years ago.[1] The rms deviation σ between calculated and experimental energy levels was 140 cm^{-1}, which is comparable to that obtained in other analyses of tetravalent actinides in cubic[2-4] and D_{2d} (Refs. 5 and 6) symmetries. All such results are very unsatisfactory when compared with those for the trivalent actinides[7] and lanthanides,[8,9] where σ's are generally of the order of 20 and 10 cm^{-1}, respectively. The large value of σ was not the only problem with the previous analysis of U^{4+}:$ThBr_4$; there were several experimental facts which remained unexplained:

(1) Even at 4 K there are more lines than can be explained by zero-phonon transitions obeying D_{2d} selection rules.

(2) At 4.2 K sharp lines (width ~1 cm^{-1}) are expected, irrespective of polarization, but for U^{4+}:$ThBr_4$, σ transitions are 40—80 cm^{-1} wide while π transitions are ~8 cm^{-1} wide.

(3) The line profiles have a form[1,10,11] not seen previously in lanthanide or actinide spectra. The lines rise and fall very steeply (edge singularities) with a small dip inbetween. σ lines usually have an additional peak located within the dip; π lines do not.

(4) Selective-excitation experiments produce fluorescence lines whose energies vary continuously with exciting wavelength.[11]

All of these features have now been explained by the fact that, at $T_c \leq 95$ K, $ThBr_4$ exists as an incommensurately modulated structure,[12] in which a sinusoidal distortion modulates the Br^- ion positions and reduces the actinide site symmetry. The line-shape analysis[10] and selective-excitation experiments[11] (hereafter referred to as I) showed that the U^{4+} ions in $ThBr_4$ occupy a range of sites which vary continuously from D_{2d} to a limiting D_2 symmetry. This allowed division of the observed peaks into those associated with U^{4+} in the D_{2d} and the limiting D_2 sites. Thus we are now in a position to analyze the energy levels of U^{4+} in both of these sites.

ANALYSIS OF THE DATA

The levels were fit by simultaneous diagonalization of the free-ion and crystal-field Hamiltonians H_f, H_c, and H_c', treating all radial terms as parameters[13]:

$$H = H_f + H_c + H_c' ,$$

where

$$H_f = \sum_{k=2,4,6} f_k F^k + \zeta_f \sum_i \vec{s}_i \cdot \vec{l}_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k=2,4,6} p_k P^k + \sum_{k=0,2,4} m_k M^k , \tag{1}$$

$$H_c = \sum_{k=2,4,6} B_0^k C_0^k + \sum_{k=4,6} B_4^k (C_4^k + C_{-4}^k) , \tag{2}$$

$$H_c' = \sum_{k=2,4,6} B_2^k (C_2^k + C_{-2}^k) + B_6^6 (C_6^6 + C_{-6}^6) . \tag{3}$$

H_c' is the perturbation of the crystal-field Hamiltonian H_c when the symmetry is lowered from D_{2d} to D_2. Those parameters which occur in both D_{2d} and D_2 symmetries [Eq. (2)] may have different values in the two cases. In D_{2d} symmetry the crystal-field states are either singlets

TABLE I. D_2 character table correspondence between D_{2d} and D_2 representations.

	D_2 character table[a]				
	E	C_2^z	C_2^y	C_2^x	
Γ_1	1	1	1	1	
Γ_2	1	1	-1	-1	z
Γ_3	1	-1	1	-1	y
Γ_4	1	-1	-1	1	x

D_{2d} to D_2 decomposition					
D_{2d}	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
D_2	Γ_1	Γ_2	Γ_1	Γ_2	$\Gamma_3+\Gamma_4$

[a] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944).

TABLE II. Selection rules.

(a) D_{2d}

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Γ_1				π	σ
Γ_2			π		σ
Γ_3		π			σ
Γ_4	π				σ
Γ_5	σ	σ	σ	σ	

(b) D_2

	Γ_1	Γ_2	Γ_3	Γ_4
Γ_1		π	σ	σ
Γ_2	π		σ	σ
Γ_3	σ	σ		π
Γ_4	σ	σ	π	

TABLE III. Observed and calculated energy levels (cm^{-1}) for U^{4+}:ThBr$_4$ in D_{2d} sites [results of calculation (A), Table V].

Γ	E_{calc}	E_{obs}	ΔE[a]	Eigenvector[b]	g_{calc}
4	0	0	0	90 $^3H_4+8\ ^1G_4$	
5	109	78	31	88 $^3H_4+9\ ^1G_4$	-0.470
1	148			88 $^3H_4+10\ ^1G_4$	
3	657			93 $^3H_4+7\ ^1G_4$	
2	707			89 $^3H_4+9\ ^1G_4$	
1	864			87 $^3H_4+10\ ^1G_4$	
5	980	943	37	87 $^3H_4+10\ ^1G_4$	4.138
3	3704			80 $^3F_2+16\ ^1D_2$	
5	3863			75 $^3F_2+12\ ^1D_2$	-1.562
4	3942			85 $^3F_2+12\ ^1D_2$	
1	4025			81 $^3F_2+12\ ^1D_2$	
3	5624			95 $^3H_5+3\ ^3F_3$	
5	5727	5730	-3	91 $^3H_5+4\ ^3F_2$	-0.783
2	5790			97 $^3H_5+2\ ^3F_3$	
4	6018			96 $^3H_5+2\ ^3F_4$	
5	6104			95 $^3H_5+2\ ^3F_4$	1.366
5	6421	6450	-29	94 $^3H_5+4\ ^3F_2$	-6.794
1	6556			93 $^3H_5+3\ ^3F_2$	
2	6561			96 $^3H_5+4\ ^3F_3$	
5	8277	8246	31	95 $^3F_3+2\ ^3H_6$	6.241
3	8307			94 $^3F_3+3\ ^3H_5$	
2	8329			88 $^3F_3+6\ ^3H_5$	
4	8390			83 $^3F_3+6\ ^3F_4$	
5	8506	8513	-7	85 $^3F_3+6\ ^3H_4$	-1.892
1	8759			47 $^3F_4+38\ ^1G_4$	
5	8829			46 $^3F_4+34\ ^1G_4$	1.362
4	8959			43 $^3F_4+25\ ^1G_4+15{}^3F_3$	
2	9086			53 $^3F_4+34\ ^1G_4$	
1	9199	9250	-51	53 $^3F_4+35\ ^1G_4$	
3	9450			60 $^3F_4+30\ ^1G_4$	
5	9483	9530	-47	51 $^3F_4+33\ ^1G_4$	3.003
4	10 587			81 $^3H_6+8\ ^1G_4$	
1	10 614	10 593	21	93 $^3H_6+5\ ^1I_6$	
5	10 668	10 658	10	84 $^3H_6+4\ ^1G_4$	1.606
3	10 773			87 $^3H_6+6\ ^1I_6$	
5	10 961			87 $^3H_6+7\ ^1I_6$	1.664
4	11 061			92 $^3H_6+5\ ^1I_6$	

($\Gamma_1,\Gamma_2,\Gamma_3,\Gamma_4$) or doublets ($\Gamma_5$). The presence of the additional Hamiltonian [Eq. (3)] lifts the degeneracy of the Γ_5 states so that the D_2 levels are all singlets. The D_2 character table and the correspondence between the two symmetries are shown in Table I.

The electric dipole radiation selection rules for D_{2d} and D_2 symmetry are shown in Table II. In this table π and σ polarizations represent radiation with the electric vector, respectively, along and perpendicular to the C_4 axis of the crystal (the c axis in the high-temperature structure) which is preserved even below the transition temperature. These tables are used below to determine the symmetry of the ground state.

In the following analysis we take as the D_2 levels those found in I by selective excitation to be associated with the A site and as the D_{2d} levels those associated with the B site. In addition, in the near-infrared region, we have identified the D_{2d} component in the σ lines by comparison with the spectrum[14] of U^{4+}:ThCl$_4$.

The line shapes in the U^{4+}:ThCl$_4$ spectrum are the same as those of U^{4+}:ThBr$_4$ except that in σ polarization there is no third peak associated with the D_{2d} site. Thus the D_{2d} lines of U^{4+}:ThBr$_4$ are those for which there is no corresponding line in the U^{4+}:ThCl$_4$ spectrum.

Several D_{2d} transitions were also identified via magnetic circular dichroism (MCD) experiments.[15] For those few π transitions where it was impossible to choose between the D_{2d} and D_2 peaks, the center of the line was chosen. Since the π transitions are narrow, the error is at most a few cm^{-1}. The D_{2d} levels are given in Table III and the D_2 levels in Table IV.

Since the few previous analyses of tetravalent actinides in crystals were not very satisfactory, we had few guidelines regarding the expected values of the free-ion parameters. Initial F^k and ζ values were obtained by scaling pseudorelativistic Hartree-Fock values (HFR) obtained with the program of Cowan and Griffin.[16] The calculated free ion F^2 is 74 300 cm^{-1}; we expected to find

TABLE III. (*Continued.*)

Γ	E_{calc}	E_{obs}	ΔE^{a}	Eigenvector$^{\text{b}}$	g_{calc}
3	11 137			91 ${}^3H_6+6\ {}^1I_6$	
2	11 142			91 ${}^3H_6+7\ {}^1I_6$	
1	11 451			84 ${}^3H_6+7\ {}^1I_6$	
5	11 828			87 ${}^3H_6+7\ {}^1I_6$	−10.254
3	14 313			51 ${}^1D_2+31\ {}^3P_2$	
4	14 358			47 ${}^1D_2+38\ {}^3P_2$	
1	14 392	14 368	24	41 ${}^3P_0+19\ {}^1D_2+17\ {}^3P_2+7\ {}^1G_4$	
5	14 632	14 654	−22	48 ${}^1D_2+35\ {}^3P_2$	−2.101
1	14 940	14 899	41	45 ${}^3P_0+27\ {}^1D_2+19\ {}^3P_2$	
1	15 229	15 204	25	47 ${}^3F_4+40\ {}^1G_4$	
5	15 389	15 412	−23	47 ${}^1G_4+48\ {}^3F_4$	−1.936
2	15 587			51 ${}^1G_4+38\ {}^3F_4$	
1	15 821			48 ${}^1G_4+41\ {}^3F_4$	
4	15 867			52 ${}^1G_4+41\ {}^3F_4$	
5	16 052	16 003	49	51 ${}^1G_4+42\ {}^3F_4$	2.256$^{\text{c}}$
3	16 667			57 ${}^1G_4+35\ {}^3F_4$	
2	17 001	16 997	4	94 ${}^3P_1+4\ {}^3F_4$	
5	17 313	17 335	−22	97 ${}^3P_1+1\ {}^1D_2$	−3.015$^{\text{d}}$
1	19 285	19 311	−26	88 ${}^1I_6+8\ {}^3H_6$	
5	19 344	19 341	3	91 ${}^1I_6+8\ {}^3H_6$	0.017
3	19 433			84 ${}^1I_6+6\ {}^3H_4$	
5	19 991	19 970	21	93 ${}^1I_6+7\ {}^3H_4$	−2.000
4	20 023			81 ${}^1I_6+12\ {}^3P_2$	
2	20 027			91 ${}^1I_6+6\ {}^3H_6$	
5	20 387	20 382	7	92 ${}^1I_6+6\ {}^3H_6$	−4.091
1	20 446	20 460	−14	91 ${}^1I_6+5\ {}^3H_6$	
3	20 827			63 ${}^1I_6+22\ {}^3P_2$	
4	20 938			85 ${}^1I_6+6\ {}^3P_2$	
3	21 558			38 ${}^3P_2+35\ {}^1I_6+23\ {}^1D_2$	
5	21 813	21 842	−29	61 ${}^3P_2+35\ {}^1D_2$	−2.634
1	22 229	22 220	9	57 ${}^3P_2+37\ {}^1D_2$	
4	22 306			40 ${}^3P_2+35\ {}^1D_2+20\ {}^1I_6$	
1	38 522			93 ${}^1S_0+7\ {}^3P_0$	

[a] $\Delta E = E_{\text{calc}} - E_{\text{obs}}$.

[b] Eigenvectors are given with the percentage of each *SLJ* level. Enough components (at least 2) are given to account for 90% of each state.

[c] $|g_{\text{expt}}| = 2.1$.

[d] $|g_{\text{expt}}| = 2.6$.

$F^2 \sim 55$—60% of this value. [For U^{3+}:$LaCl_3$, $F^2=0.56 \times F^2$ (HFR), for example.[7]] Similar reasoning led us to expect $\zeta \sim 1770$ cm^{-1}. We initially set α, β, and γ at the U^{4+} free-ion values.[17]

Diagonalization of the free-ion levels with these parameters showed that the $^3P_1$ is well separated from other levels but the $^3P_0$, $^1D_2$, and $^1G_4$ are close together and likely to be mixed by a large crystal field. Thus we can establish the D_{2d} level at 17 335 cm^{-1} as the Γ_5 component of the $^3P_1$ multiplet.

The position of the Γ_2 component of $^3P_1$ multiplet was established as follows. There is a temperature-dependent absorption at 16 996 cm^{-1} which is not correlated with a temperature-independent line.[14] We assume that this absorption line corresponds to a transition, allowed from the D_2 level at 10 cm^{-1}, but forbidden from the D_{2d} ground state. The corresponding fluorescence lines to both the 10-cm^{-1} level and to the D_{2d}-Γ_5 at 78 cm^{-1} are observed (see I). Since the $^3P_1$ is the only multiplet in this energy range, we assign the absorption at 16 996 cm^{-1} to its D_2-Γ_2 component. The corresponding D_{2d} level at 16 997 cm^{-1} is assigned to the Γ_2 of the $^3P_1$ multiplet.

We can now determine the symmetry of the D_{2d} ground state. We know from I that the ground state is a singlet and the lack of a π transition to $^3P_1$ rules out Γ_3 (see Table II). To choose between the $\Gamma_{1,2}$ and the Γ_4 levels one must look at the J-mixed group corresponding to $^1D_2$, $^3P_0$, and $^1P_4$ multiplets. For a $\Gamma_{1,2}$ ground state we expect two π transitions; for a Γ_4 ground state we expect four. Four intense transitions are observed. Therefore, we conclude that the ground state is a Γ_4 level. This is the same ground state chosen in Ref. 1, but it was previously chosen because U^{4+} has a Γ_4 ground state in other crystals of D_{2d} symmetry. In D_2 symmetry the ground state becomes Γ_2 (see Table I).

D_{2d} SYMMETRY CALCULATIONS

Using the estimated free-ion parameters, we initially diagonalized the matrices with various values of B_0^2. Only $B_0^2 \sim -1000$ cm^{-1} gave approximately the correct separation between the $^3P_1$ Γ_2 and Γ_5 levels. Given this B_0^2 value, we tried various values of B_0^4; only $B_0^4 \sim 1000$ cm^{-1} gave the Γ_4 and Γ_3 states (degenerate in this approximation) as the ground state with the Γ_5 state at almost the same energy. A negative B_4^4 along with a positive B_4^6 gives a Γ_4 ground state, whereas changing both signs changes Γ_4 to Γ_3 without changing the energies. Thus we were led rather quickly to the signs and order of magnitude of these parameters. The calculations plus polarization studies could then be used to make further assignments of Γ_1 and Γ_5 levels and to refine the least-squares fit.

Since the large spin-orbit and crystal-field interactions cause considerable mixing of states and F^4 and F^6 are frequently not well determined, we tried initially to prevent spurious results by fixing ratios $F^4/F^2 \sim 0.85$ and $F^6/F^2 \sim 0.56$—0.6 as found for the trivalent actinides[8] and for the U^{4+} free ion[17–19]; the fits were always very poor, $\sigma > 100$ cm^{-1}. But as soon as the F^k's were allowed to vary independently the fit improved greatly.

Initially we used the recent U^{4+} free-ion results[17] to fix γ and the P^k and M^k parameters. In the crystal the value of γ is determined by the position of the $^3P_0$ level (through its $\sim 2\%$ $^1S_0$ component). The P^k's determine the relative splittings of the $^3P_{0,1,2}$ levels. Fitting γ will make the $^3P_0$ fit very well but the value of γ depends on the values used for the P^k's. When we fixed γ at 800 cm^{-1} and all of the P^k's at 500 cm^{-1} (approximately their free-ion values), we obtained for 26 levels a rms deviation σ of 41 cm^{-1}. Increasing γ to 1200 cm^{-1}, closer to the values found for the trivalent actinides in crystals, gives $\sigma = 36$ cm^{-1}. If γ is allowed to vary freely, it is ~ 2000 cm^{-1} but σ is decreased by only ~ 1 cm^{-1}. Without the position of the $^1S_0$ we must regard both the P^k and γ parameters as only approximately determined.

The energy levels in Table III (calculated with $\gamma = 1200$ cm^{-1}) show that the strongly fluorescing $^3P_0$ level at 14 368 cm^{-1} is not the level immediately above a large energy gap. The unobserved Γ_3 and Γ_4 components of the $^1D_2$-$^3P_2$ multiplet lie lower. Since it is always the lowest level in a group which fluoresces, the Γ_3 and Γ_4 levels are calculated at too low an energy. All of these levels are quite sensitive to the values of γ, the P^k's, and ζ. At the moment we cannot rule out the possibility that if the position of the $^1S_0$ were known so as to establish γ, values of the other parameters could be found which would put the $^3P_0$ below the $^1D_2$-$^3P_2$ levels.

The results given in Table III show that while many levels fit very well, there are five levels for which the deviation between experimental and calculated levels is greater than 36 cm^{-1}. Four of these five levels have eigenvectors which are mixtures of $^1G_4$ and ^{3}F or ^{3}H components, and the largest deviations are for levels which are nearly equal mixtures of $^1G_4$ and $^3F_4$.

The conjecture that somewhat different parameters are needed for the $^1G_4$ level than for the ^{3}H and ^{3}F levels led us to consider an extension of the crystal-field Hamiltonian as suggested by Judd[20] and Newman *et al.*[21] They have shown that spin correlation and some covalency effects can be accommodated simply by making the following replacements in the reduced matrix elements of the crystal-field operators:

$$(\psi||U^{(k)}||\psi')\rightarrow(\psi||U^{(k)}||\psi')+c_k[S(S+1)/(2S+1)]^{1/2}(\psi||V^{(1k)}||\psi') \tag{4}$$

(Ref. 20) or

$$(\psi||U^{(k)}||\psi')\rightarrow\{1+[-\tfrac{3}{4}\pm\tfrac{1}{2}(S_M+1)]c_k\}(\psi||U^{(k)}||\psi')+c_k\{[S(S+1)/(2S+1)]^{1/2}(\psi||V^{(1k)}||\psi') \pm(S_M+1)(\psi||U^{(k)}||\psi')\}\ , \tag{5}$$

TABLE IV. Observed and calculated energy levels (cm^{-1}) for U^{4+}:ThBr$_4$ in the limiting D_2 sites.

Γ	E_{calc}	E_{obs}	ΔE	Γ	E_{calc}	E_{obs}	ΔE
2	0	0	0	3	10 882		
3	73	10	63	4	11 001		
4	166	146	20	2	11 017		
1	171			1	11 097		
1	657			2	11 121		
2	727			1	11 444		
1	881			3	11 830		
3	994	967	27	4	11 864		
4	1020	1010	10	1	14 276		
1	3707			2	14 329		
3	3849			1	14 409	14 364	45
4	3860			4	14 601	14 612	−11
2	3943			3	14 646	14 709	−63
1	4037			1	14 969	14 915	54
1	5608			1	15 211	15 207	5
4	5707	5726	−19	3	15 394	15 392	2
3	5728	5734	−6	4	15 396	15 421	−25
2	5778			2	15 591		
2	5995			1	15 817		
4	6054			2	15 926		
3	6107			4	16 047	16 003	44
4	6384	6328	56	3	16 058	16 013	45
3	6436			1	16 720		
1	6558			2	17 017	17 006	11
2	6561			4	17 320	17 347	−27
3	8247	8246	1	3	17 356	17 368	−12
4	8262	8248	14	1	19 293	19 302	−9
1	8288			3	19 330	19 318	12
2	8307			4	19 382	19 352	30
2	8386			1	19 454		
3	8498	8470	28	4	19 913	19 942	−29
4	8507	8552	−45	2	19 971		
1	8779			3	20 086		
3	8827			2	20 091		
4	8865			3	20 349		
2	8961			4	20 449		
2	9106			1	20 454	20 460	−6
1	9207	9250	−43	1	20 871		
1	9459	9499	−40	2	20 980		
4	9499	9530	−31	1	21 568		
3	9510	9560	−50	4	21 728		
2	10 570			3	21 847	21 838	9
1	10 576	10 584	−8	1	22 225	22 220	5
3	10 647	10 652	−5	2	22 318		
4	10 669	10 656	13	1	38 680		
1	10 753						

(Ref. 21), where S_M is the maximum spin of f^N and the upper signs refer to less than half-filled shells. The parameters c_k have been estimated at a few tenths for the lanthanide cases considered.[20,21] The signs of the c_k's depend on the particular mechanism being considered.

Since the reduced matrix elements of $V^{(1k)}$ are zero for singlets of f^2 and proportional to those of $U^{(k)}$ for triplets, both of the replacements (4) and (5) have the effect of allowing singlets and triplets to have different parameters, which we designate $B_q^k(S)$ and $B_q^k(T)$. The lack of q dependence in (4) and (5) requires the restriction that

$$\frac{B_q^k(T)}{B_{q'}^k(T)}=\frac{B_q^k(S)}{B_{q'}^k(S)} \; . \tag{6}$$

The parameters of Table V show $B_4^6/B_0^6=-0.22$ and $B_4^4/B_0^4=-1.69$. With B_4^6/B_0^6 fixed at various values between -0.1 and -0.4, singlet and triplet states were al-

TABLE V. Parameters (cm^{-1}) for U^{4+}:$ThBr_4$ in D_{2d} and limiting D_2 sites and for the U^{4+} free ion.

	U^{4+}:$ThBr_4$			Free ion[a]	
	D_{2d}		D_2		
	Calc. (A)	Calc. (B)		Calc. (A)	Calc. (B)
F^2	42 253±127	41 800± 87	42 264± 84	51 938 ± 39	51 294± 35
F^4	40 458±489	40 488±445	41 159±407	42 708 ±100	42 414±108
F^6	25 881±383	28 069±218	26 018±237	27 748 ± 68	29 907± 66
ζ	1783± 7	1783± 5	1774± 5	1968 ± 2	1968± 2
α	31± 1		(31)	35.5± 0.4	
β	−644± 75		(−644)	−664 ± 25	
γ	(1200)[b]		(1200)	744 ± 26	
α'		(24.6)			28.4±0.3
β'		(−15.86)			−31±3
γ'		(102.3)			72±2
M^0	(0.99)	(0.99)	(0.99)	(0.99)	(0.99)
M^2	(0.55)	(0.55)	(0.55)	(0.55)	(0.55)
M^4	(0.38)	(0.38)	(0.38)	(0.38)	(0.38)
P^2	(500)	(500)	(500)	573 ± 66	574± 66
P^4	(500)	(500)	(500)	524 ±144	524±144
P^6	(500)	(500)	(500)	1173 ±321	1174±320
B_0^2	−1096± 80	−1.096± 63	−1108± 65		
B_0^4	1316±146	1316±134	1358±137		
B_4^4	−2230± 85	−2231± 77	−2219± 76		
B_0^6	−3170±379	−3170±327	−3458±267		
B_4^6	686±246	684±216	694±195		
B_2^2			−78± 30		
B_2^4			318±122		
B_2^6			136±101		
B_6^6			123±125		
Number of levels	26		38	13	13
σ	36		39	9.8	9.8

[a] From Ref. 17.

[b] Parameters in parentheses were held fixed in the fitting procedure.

lowed to have different values of B_0^6. σ quickly increased as the ratio departed from −0.22 and $B_0^6(T)$ remained nearly equal to $B_0^6(S)$. Similar results were obtained when $B_0^4(S)$ and $B_0^4(T)$ were allowed to be different but with B_4^4/B_0^4 fixed at values between −1 and −2. Thus it seems that any new parametrization of the form given by Eq. (4) or (5) cannot account for the large differences between some of the experimental and calculated levels of U^{4+}:$ThBr_4$.

D_2 SYMMETRY CALCULATIONS

Since the effects of the incommensurate structure which lowers the symmetry from D_{2d} to D_2 are presumed to be small, we adopted the following strategy to determine the D_2 crystal-field parameters.

(1) The D_2 levels were treated as D_{2d} by fixing the parameters of Eq. (1) and fitting those of Eq. (2) to the D_2 Γ_1 levels and the centers of gravity of the Γ_3-Γ_4 pairs (Γ_5 in D_{2d}).

(2) Each experimental Γ_3-Γ_4 pair was adjusted to give the calculated centers of gravity so that the variation of the parameters in H_c' [Eq. (3)] would fit only the Γ_3-Γ_4 splittings and not the centers of gravity. The initial B_2^2 was chosen to give approximately the correct splitting for the $^3P_1$ Γ_3-Γ_4 pair. The other parameters were initially zero. A change in the sign of B_2^2 results in a sign change for all of the other parameters. B_6^6 was poorly determined, consistent with zero.

(3) With the parameters of step (2) as initial values, the Slater parameters, ζ, and all of the crystal-field parameters were allowed to vary. This resulted in $\sigma = 39\ \mathrm{cm}^{-1}$ for 38 levels as shown in Tables IV and V.

For both the free-ion and crystal-field parameters of Eq. (2) the differences between the D_2 and D_{2d} results are much smaller than the rms errors on the parameters. The D_2 parameters of Eq. (3) are all very small, ~10% of the D_{2d} parameters, as expected from the small amplitude of the modulation.[12] As in the D_{2d} case, the levels which fit poorly are mixtures of $^1G_4$ and $^3F_4$. The largest deviation for the Γ_3-Γ_4 splittings is 73 cm^{-1} (Table IV). In general the calculated splittings are too small.

DISCUSSION

For ions with d^N configurations, the F^k's are usually replaced by the Racah parameters B and C; free-ion (FI) and crystal values of the Racah parameter B are often compared[22] via the ratio $\beta = B_{\mathrm{cryst}}/B_{\mathrm{FI}}$. We introduce here the equivalent ratios $\phi_k = F^k_{\mathrm{cryst}}/F^k_{\mathrm{FI}}$, $Z = \zeta_{\mathrm{cryst}}/\zeta_{\mathrm{FI}}$, and also $r_{42}=F^4/F^2$. For U^{4+}:$ThBr_4$ we find $\phi_2=0.81$, $\phi_4=0.95$, and $\phi_6=0.92$, i.e., F^2 is reduced much more than F^4 and F^6 on going from the free ion to the crystal. We can compare these results with the Pr^{3+}:$LaCl_3$ case,[8,19] where $\phi_2=0.93$ and $\phi_4=0.97$. For U^{4+}:$ThBr_4$, $Z=0.91$ whereas for Pr^{3+}:$LaCl_3$ it is 0.98. For U^{4+}:$ThBr_4$, r_{42} is increased to 0.96 (compared to 0.82 for the free ion); the equivalent ratios in Pr^{3+}:$LaCl_3$ are 0.73 and 0.70. The effect of the transition from free ion to crystal on the parameters of U^{4+} is much greater than it is for Pr^{3+}.

For d transition-metal ions in various crystals, the values of r_{42} are increased from the free-ion values and values of $\phi_2 \sim 0.8$ are commonly found. Our U^{4+} values are similar to those found for $Cr^{3+}(3d^3)$ in emerald or K_2NaCrF_6 or $Co^{2+}(3d^7)$ in $CoCl_2$.[23,24] The range of r_{42} and ϕ_2 values for $3d$ transition-metal ions in crystals is very large, however, with r_{42} increasing and ϕ_2 decreasing as the ligand changes from F^- to Cl^- to Br^-.[23–25] Our values for U^{4+} with a bromide ligand are similar to those for a trivalent $3d$ ion with fluoride ligands or a divalent ion with chloride ligands. (Since there are no free-ion analyses for $5f^N$ in the fourth spectra of the actinides, we can make no comparison between trivalent and tetravalent actinides.)

In discussions of d^N spectra, β (here ϕ_2) less than 1 is commonly attributed to effects of covalency.[22] Newman[25] has argued that the variation in F^2 from host to host should rather be correlated with the ligand polarizability α and that the mechanism for the decrease in F^2 is the same for the d transition metals, lanthanides, and actinides. Morrison[26] has given an expression (corrected by Eremin and Kornienko[27]) for the decrease in the Slater parameters due to the polarizability of the ligands:

$$\Delta F^k = -e^2 \sum_i \frac{\alpha_i Z_i}{R_i^{2k+4}} \langle r^k \rangle_f^2 (k+1) , \tag{7}$$

where Z_i is the number of ligands of polarizability α_i at a distance R_i from the metal ion. Equation (7) does qualitatively predict $\phi_2 < \phi_4 < \phi_6$. Eremin and Kornienko[27] have shown that ligand polarizability accounts for only a 0.4% decrease in F^2 compared to a 10% observed decrease for Ni^{2+} (NiF_6^{4+}) and Mn^{2+} (MnF_6^{4+}) in fluoride crystals. From Eq. (7), the Dirac-Slater $\langle r^2 \rangle^{++}$ value of Lewis *et al.*[28] (chosen to give the maximum effect), and with all $R_i = 3$ Å,[29] we find $\Delta F^2 \simeq -660$ cm^{-1} for U^{4+}:$ThBr_4$. This is only 7% of the observed decrease from the free-ion value.

From empirical correlations Newman[25] found, for Pr^{3+} and U^{4+}, $\Delta F^2 = -968\alpha$ and $\Delta F^2 = -1530\alpha$, respectively, i.e., F^2 is much more sensitive to ligand polarizability for U^{4+} than for Pr^{3+}. For U^{4+}:$ThBr_4$ this relationship predicts $\Delta F^2 = -6365$ cm^{-1}, 66% of the observed effect. But this result is questionable because of the uncertainties in the U^{4+} analyses from which Newman's equation was derived. (All of the rms deviations are too large to guarantee that the correct set of parameters has been found.)

We see that while the empirical correlation with ligand polarizability seems to account for the trend and the order of magnitude of the decrease in F^k, Eq. (7) gives an effect which is much too small.

Judd *et al.*[30] have recently defined new configuration interaction parameters α', β', and γ' whose matrix elements are orthogonal to those of the Slater integrals. Except for nonlinear effects arising from spin-orbit coupling, the parameters are then all independent. Thus the Slater parameters will not change with the inclusion or exclusion of γ as they do in the usual parametrization scheme. Use of α', β', and γ' should reduce the rms errors in the parameters and thereby facilitate the extrapolation from one ion to another.

The old and new parameters are related by[31]

$$\begin{aligned} \alpha' &= \tfrac{4}{5}\alpha , \\ \beta' &= -4\alpha - \beta/6 , \\ \gamma' &= \tfrac{8}{5}\alpha + \beta/15 + 2\gamma/25 . \end{aligned} \tag{8}$$

The Slater parameters, particularly F^6, depend on which set of configration interaction parameters are used. The D_{2d} calculation was repeated with α', β', and γ' fixed by Eq. (8) in order to establish the differences in the Slater parameters. The results are shown as calculation (B) in Table V. The corresponding free-ion results are also shown for comparison. Use of these parameters changes the ratios discussed above by less than 0.01 and makes no difference in the conclusions.

CONCLUSIONS

We have used the crystal-field model to successfully interpret the energy levels of U^{4+} in both D_{2d} and D_2 sites in a modulated structure. The results are somewhat poorer than for trivalent actinides and, as in those cases, there are some rather large deviations between calculated and experimental levels. Most of these are associated with levels in which there is strong mixing between $^1G_4$ and ^3F and ^3H levels. The spin-polarization mechanism previously suggested to account for some large deviations in the lanthanides will not account for the large deviations found here.

Further work is needed to provide a detailed understanding of the reasons for the larger deviations from the crystal-field model for the actinides than for the lanthanides.

Both the large spin-orbit and crystal-field interactions result in a great deal of mixing between *SLJ* states, and the crystal field cannot be regarded as a perturbation of the free-ion states. Changes in either the crystal-field or free-ion parameters may have similar effects on the energy of a level, although the eigenvectors may be different in the two cases. Unless there is a systematic variation of the free-ion parameters, and/or their relationships, from host to host, the results of any single fit are quite possibly spurious, especially when σ is large (greater than or equal to 100 cm^{-1}). It is clear that the relationships which hold for lanthanides and trivalent actinides are not applicable to the tetravalent actinides.

The large differences between crystal and free-ion values of F^2 and r_{42} indicate that in $ThBr_4$ the U^{4+} $5f$ electron is more like a $3d$ than a $4f$ electron. Thus the tetravalent actinides may prove to be a suitable system in which to test the various models which have been proposed to explain the changes in the free-ion parameters as the ion is placed in different hosts. The actinide variations are similar to the smallest effects seen for the $3d$ transition-metal ions and the spectra are much more amenable to a detailed analysis.

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$$\sigma=\left[\sum_i (E^i_{\mathrm{obs}}-E^i_{\mathrm{calc}})^2/(N_l-N_p)\right]^{1/2},$$

where N equals the number of levels and N_p equals the number of parameters varied.

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