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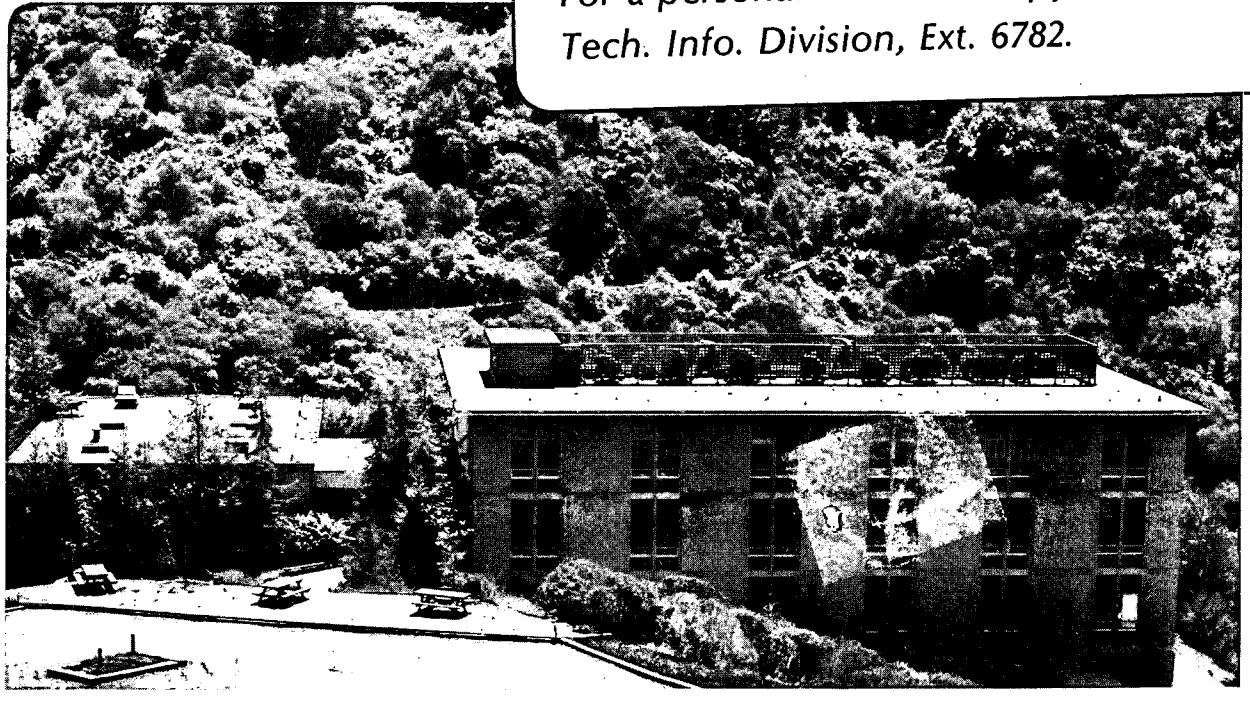

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Parametric Analysis of the Energy Levels of U^{4+} in D_{2d} and Limiting D_2 Sites in Incommensurate $ThBr_4$

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ABSTRACT

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 identified spectroscopically. We report a parametric analysis of the U^{4+} energy levels in both sites. For 26 levels in the D_{2d} site the rms deviation σ = 36 cm^{-1} and F^2 = 42253 ± 127, F^4 = 40458 ± 489, F^6 = 25881 ± 383, ζ = 1783 ± 7, α = 31 ± 1, β = -644 ± 75, γ = 1200, B_0^2 = -1096 ± 80, B_0^4 = 1316 ± 146, B_4^4 = -2230 ± 85, B_0^6 = -3170 ± 379, and B_4^6 = 686 ± 246, all in cm^{-1}. For 38 D_2 levels σ = 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 ± 30, B_2^4 = 318 ± 122, B_2^6 = 136 ± 101, B_6^6 = 123 ± 125, all in cm^{-1}. F^2 is 81 percent 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} [5,6] 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 in between. σ lines usually have an additional peak located within the dip; π lines do not.

4. Selective excitation experiments produce fluorescence lines whose energy varies continuously with exciting wave length.[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

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

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

and

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

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 (Γ_1, Γ_2, Γ_3, Γ_4) or doublets (Γ_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 infra-red 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 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 HF values (HFR) obtained with the program of Cowan and Griffin.[16] The calculated free-ion F^2 is 74300 cm^{-1}; we expected to find $F^2 \sim$ 55-60 percent of this value. (For U^{3+}:$LaCl_3$, $F^2 = 0.56\ F^2$ (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 that $^3P_1$ 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 17335 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 16996 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 multplet in this energy range, we assign the absorption at 16996 cm^{-1} to its D_2-Γ_2 component. The corresponding D_{2d} level at 16997 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

~ -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 ~ 1000 cm^{-1} gave the Γ_4 and $_3$ states (degenerate in this approximation) as the ground state with the $_5$ 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 $F^4/F^2 \sim .85$ and $F^6/F^2 \sim .56$-$.6$ 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 ~ 2 percent $^1S_0$ 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^ks at

500 cm^{-1} (approximately their free-ion values) we obtained for 26 levels an 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 σ = 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 γ = 1200 cm^{-1}) show that the strongly fluorescing $^3P_0$ level at 14368 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 ^3F or ^3H 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 ^3H and ^3F 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:

$$(\psi\|U^{(k)}\|\psi') \rightarrow (\psi\|U^{(k)}\|\psi') + c_k[S(S+1)/(2S+1)]^{1/2}\,(\psi\|V^{(1k)}\|\psi'),^{19} \quad (4)$$

or

$$\begin{aligned}(\psi\|U^{(k)}\|\psi') \rightarrow\ & [1+(-3/4 \pm 1/2(S_M+1))c_k](\psi\|U^{(k)}\|\psi') \\ & + c_k[S(S+1)/(2S+1)]^{1/2}(\psi\|V^{(1k)}\|\psi') \\ & \pm (S_M+1)(\psi\|U^{(k)}\|\psi')],^{20}\end{aligned} \quad (5)$$

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 $B^k_q(S)$ and $B^k_q(T)$. The lack of q-dependence in (4) and (5) requires the restriction that

$$\frac{B^k_q(T)}{B^k_{q'}(T)} = \frac{B^k_q(S)}{B^k_{q'}(S)} \ . \quad (6)$$

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 allowed 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 parameterization 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 $\Gamma_3 - \Gamma_4$ pairs (Γ_5 in D_{2d}).

2. Each experimental $\Gamma_3 - \Gamma_4$ 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 $\Gamma_3 - \Gamma_4$ splittings and not the centers of gravity. The initial B_2^2 was chosen to give

approximately the correct splitting for the $^3P_1$ $\Gamma_3 - \Gamma_4$ 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 $\sigma = 39$ 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 percent 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 $\Gamma_3 - \Gamma_4$ 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 $\beta = B_{crystal}/B_{FI}$. We introduce here the equivalent ratios $\phi_k = F^k_{crystal}/F^k_{FI}$, $Z = \zeta_{crystal}/\zeta_{FI}$, and also $r_{42} = F^4/F^2$. For U^{4+}:$ThBr_4$ we find $\phi_2 = .81$, $\phi_4 = .95$, and $\phi_6 = .92$, 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 .96 (compared to .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) < 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:

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

where Z_i is the number of ligands of polarizability α_i at a distance R_i from the metal ion. Eq. (7) does qualitatively predict $\phi_2 < \phi_4 < \phi_6$. Eremin and Kornienko[27] have shown that ligand polarizability accounts for only a .4 percent decrease in F^2 compared to a 10 percent 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 percent 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 percent 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 non-linear 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 parameterization scheme. Use of α', β' and γ' should reduce the rms errors on the parameters and thereby facilitate the extrapolation from one ion to another.

The old and new parameters are related by[31]

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

The Slater parameters, particularly F^6, depend on which set of configuration 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 calc. B in Table V. The corresponding free-ion results are also shown for comparison. Use of these parameters changes the ratios discussed above by $< .01$ 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 ($\geq$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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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	
1	1	1	1	1	
2	1	1	-1	-1	z
3	1	-1	1	-1	y
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] Henry Eyring, John Walter, George E. Kimball, Quantum Chemistry, John Wiley and Sons, Inc., 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[a]

Γ	E_{calc}	E_{obs}	ΔE[b]	Eigenvector[c]	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 $^1G_4$	–

Table III continued

Γ	E_{calc}	E_{obs}	ΔE[b]	Eigenvector[c]	g_{calc}
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	10587	–	–	81 $^3H_6$ + 8 $^1G_4$	–
1	10614	10593	21	93 $^3H_6$ + 5 $^1I_6$	–
5	10668	10658	10	84 $^3H_6$ + 4 $^1G_4$	1.606
3	10773	–	–	87 $^3H_6$ + 6 $^1I_6$	–
5	10961	–	–	87 $^3H_6$ + 7 $^1I_6$	1.664
4	11061	–	–	92 $^3H_6$ + 5 $^1I_6$	–
3	11137	–	–	91 $^3H_6$ + 6 $^1I_6$	–
2	11142	–	–	91 $^3H_6$ + 7 $^1I_6$	–
1	11451	–	–	84 $^3H_6$ + 7 $^1I_6$	–
5	11828	–	–	87 $^3H_6$ + 7 $^1I_6$	-10.254
3	14313	–	–	51 $^1D_2$ + 31 $^3P_2$	–
4	14358	–	–	47 $^1D_2$ + 38 $^3P_2$	–
1	14392	14368	24	41 $^3P_0$ + 19 $^1D_2$ + 17 $^3P_2$ + 7 $^1G_4$	–
5	14632	14654	-22	48 $^1D_2$ + 35 $^3P_2$	-2.101
1	14940	14899	41	45 $^3P_0$ + 27 $^1D_2$ + 19 $^3P_2$	–
1	15229	15204	25	47 $^3F_4$ + 40 $^1G_4$	–
5	15389	15412	-23	47 $^1G_4$ + 48 $^3F_4$	-1.936
2	15587	–	–	51 $^1G_4$ + 38 $^3F_4$	–
1	15821	–	–	48 $^1G_4$ + 41 $^3F_4$	–
4	15867	–	–	52 $^1G_4$ + 41 $^3F_4$	–
5	16052	16003	49	51 $^1G_4$ + 42 $^3F_4$	2.256[d]
3	16667	–	–	57 $^1G_4$ + 35 $^3F_4$	–
2	17001	16997	4	94 $^3P_1$ + 4 $^3F_4$	–

Table III continued

Γ	E_{calc}	E_{obs}	ΔE[b]	Eigenvector[c]	g_{calc}
5	17313	17335	-22	$97\ ^3P_1 + 1\ ^1D_2$	-3.015[e]
1	19285	19311	-26	$88\ ^1I_6 + 8\ ^3H_6$	-
5	19344	19341	3	$91\ ^1I_6 + 8\ ^3H_6$	0.017
3	19433	-	-	$84\ ^1I_6 + 6\ ^3H_4$	-
5	19991	19970	21	$93\ ^1I_6 + 7\ ^3H_4$	-2.000
4	20023	-	-	$81\ ^1I_6 + 12\ ^3P_2$	-
2	20027	-	-	$91\ ^1I_6 + 6\ ^3H_6$	-
5	20387	20382	7	$92\ ^1I_6 + 6\ ^3H_6$	-4.091
1	20446	20460	-14	$91\ ^1I_6 + 5\ ^3H_6$	-
3	20827	-	-	$63\ ^1I_6 + 22\ ^3P_2$	-
4	20938	-	-	$85\ ^1I_6 + 6\ ^3P_2$	-
3	21558	-	-	$38\ ^3P_2 + 35\ ^1I_6 + 23\ ^1D_2$	-
5	21813	21842	-29	$61\ ^3P_2 + 35\ ^1D_2$	-2.634
1	22229	22220	9	$57\ ^3P_2 + 37\ ^1D_2$	-
4	22306	-	-	$40\ ^3P_2 + 35\ ^1D_2 + 20\ ^1I_6$	-
1	38522	-	-	$93\ ^1S_0 + 7\ ^3P_0$	-

a Results of calc. A, Table V

b $\Delta E = E_{calc} - E_{obs}$.

c Eigenvectors are given with the percentage of each SLJ level. Enough components (at least 2) are given to account for 90 percent of each state.

d $|g_{exp}| = 2.1$.

e. $|g_{exp}| = 2.6$.

Table IV. Observed and calculated energy levels (cm^{-1}) for U^{4+}:$ThBr_4$ in the limiting D_2 sites

Γ^a	E_{calc}	E_{obs}	ΔE
2	0	0	0
3	73	10	63
4	166	146	20
1	171	-	-
1	657	-	-
2	727	-	-
1	881	-	-
3	994	967	27
4	1020	1010	10
1	3707	-	-
3	3849	-	-
4	3860	-	-
2	3943	-	-
1	4037	-	-
1	5608	-	-
4	5707	5726	-19
3	5728	5734	-6
2	5778	-	-
2	5995	-	-
4	6054	-	-
3	6107	-	-
4	6384	6328	56
3	6436	-	-
1	6558	-	-
2	6561	-	-
3	8247	8246	1
4	8262	8248	14
1	8288	-	-
2	8307	-	-

Table IV continued

Γ^a	E_{calc}	E_{obs}	ΔE
2	8386	-	-
3	8498	8470	28
4	8507	8552	-45
1	8779	-	-
3	8827	-	-
4	8865	-	-
2	8961	-	-
2	9106	-	-
1	9207	9250	-43
1	9459	9499	-40
4	9499	9530	-31
3	9510	9560	-50
2	10570	-	
1	10576	10584	-8
3	10647	10652	-5
4	10669	10656	13
1	10753	-	-
3	10882	-	-
4	11001	-	-
2	11017	-	-
1	11097	-	-
2	11121	-	-
1	11444	-	-
3	11830	-	-
4	11864	-	-
1	14276	-	-
2	14329	-	-
1	14409	14364	45
4	14601	14612	-11
3	14646	14709	-63
1	14969	14915	54

Table IV continued

Γ^a	E_{calc}	E_{obs}	ΔE
1	15211	15207	5
3	15394	15392	2
4	15396	15421	-25
2	15591	-	-
1	15817	-	-
2	15926	-	-
4	16047	16003	44
3	16058	16013	45
1	16720	-	-
2	17017	17006	11
4	17320	17347	-27
3	17356	17368	-12
1	19293	19302	-9
3	19330	19318	12
4	19382	19352	30
1	19454	-	-
4	19913	19942	-29
2	19971	-	-
3	20086	-	-
2	20091	-	-
3	20349	-	-
4	20449	-	-
1	20454	20460	-6
1	20871	-	-
2	20980	-	-
1	21568	-	-
4	21728	-	-
3	21847	21838	9
1	22225	22220	5
2	22318	-	-
1	38680	-	-

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	
	D_{2d}		D_2		
	Calc A	Calc B		Calc A	Calc B
F^2	42253 ± 127	41800 ± 87	42264 ± 84	51938 ± 39	51294 ± 35
F^4	40458 ± 489	40488 ± 445	41159 ± 407	42708 ± 100	42414 ± 108
F^6	25881 ± 383	28069 ± 218	26018 ± 237	27748 ± 68	29907 ± 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]	-	[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	-1096 ± 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

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