Crystal-field calculations for energy levels of U^{4+} in $ZrSiO_4$

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A crystal-field calculation has been made for the energy levels of an ion with an f^2 configuration in a D_{2d} crystal field, appropriate to U^{4+} in zircon, $ZrSiO_4$. A previous analysis is found to be incorrect. The present analysis, using ten parameters, gives an energy-level fit which has a standard deviation of 112 cm^{-1} relative to 30 observed levels. This fit is comparable to those obtained by other workers for U^{4+} in octahedral and tetrahedral symmetries. Zeeman experiments and magnetic-circular-dichroism measurements have yielded g values for a number of the σ-polarized absorption lines. The values of the parameters for the best fit are (in units of cm^{-1}): $F_2 = 196.7$, $F_4 = 37.0$, $F_6 = 4.25$, $\zeta = 1740$, $\alpha = 22.8$, $A_2^0\langle r^2\rangle = -1000$, $A_4^0\langle r^4\rangle = 250$, $A_4^4\langle r^4\rangle = 5360$, $A_6^0\langle r^6\rangle = -362$, and $A_6^4\langle r^6\rangle = -300$.

I. INTRODUCTION

The optical spectra of the actinide ions, incorporated as isolated ions in crystals, are not nearly as well understood as those of the lanthanides or $3d$ elements. The main problem is that, unlike the situation for the lanthanides and $3d$ elements, the energies of the crystal-field, interelectron-repulsion, and spin-orbit interactions are all comparable. Thus optical transitions for actinides are not observed as closely spaced line groups at energies which are mainly determined by either crystal-field or spin-orbit interactions.

The most widely studied actinide ion is U^{4+}, since the f^2 configuration is the simplest case in which there are more energy levels than parameters, using the crystal-field model. The 91×91 matrix for the f^2 configuration can be readily diagonalized using modern computers. Crystal-field calculations for U^{4+} in zircon have been reported by Richman *et al.*[1]—hereafter referred to as RKW. The metal site symmetry in zircon is D_{2d}, which is noncentrosymmetric, so that electric dipole transitions are not parity forbidden. The initial aim of the present work was to reproduce the RKW calculations and then to see how the calculated g values of the electronic levels compared with values derived from Zeeman and magnetic-circular-dichroism measurements. However, attempts to reproduce the RKW calculation were unsuccessful and it was concluded that their calculation was incorrect. The method used in the present work has been described previously by Gerloch and Mackey,[2] and merely by changing the reduced matrix elements and interelectron-repulsion parameters[3] and the coefficients of the spherical-harmonic operators,[4,5] it is possible, in principle, to diagonalize the complete matrix for any electronic configuration in any symmetry and, therefore, to test the method with respect to a wide range of published data. The energy levels have been reproduced in the following systems: f^{13} in D_{3d} symmetry,[6] f^2 in O_h symmetry—quantized either around a threefold[7] or a fourfold[8] axis, d^2 in O_h (Ref. 9) and D_{4h} (Ref. 10) symmetries, d^3 in O_h (Ref. 11) and D_{3d} (Ref. 12) symmetries, d^4 in O_h symmetry[13] and d^5 in O_h symmetry.[14]

II. EXPERIMENTAL

Preliminary absorption spectra over the 4000–30 000-cm^{-1} range were measured with a Cary 17 spectrophotometer at temperatures down to 15 K, using a cold-gas flow tube. Absorption measurements over the 1400–4200-cm^{-1} range were carried out at 40–300 K using a double-beam Perkin-Elmer Model 180 spectrometer. Photographic and photoelectric Zeeman measurements, over the 9000–25000-cm^{-1} and 6000–25000-cm^{-1} ranges, respectively, were carried out with the sample maintained in the 5–60-K range inside an Oxford Instruments superconducting solenoid, which was capable of providing a magnetic field of 7.7 T. Other Zeeman experiments were conducted with a pulsed magnetic field of about 20 T, supplied by the large magnet in the Magnet Laboratory in the Department of Engineering Physics. Photographic detection was used, and these latter experiments were confined to the 14000–25000-cm^{-1} range.

Magnetic-circular-dichroism (MCD) spectra were measured with a Cary 61 spectropolarimeter at energies above about 12500 cm^{-1}, using the superconducting solenoid. For samples about 2 mm thick, reliable results could be obtained only when the c axis was aligned within about 2° of the direction of propagation of the light beam. Samples of about 0.3-mm thickness were used in the measurements reported here, and the tolerable misorientation was ~10°, as found by zero-field measurements with and without the specimen in series with an optically active liquid. For samples which were annealed and satisfactorily aligned, no zero-field

circular dichroism was detected, even at the energies of the strong absorptions. Some further MCD data were obtained in the 8800–11500-cm^{-1} range using equipment described by Wong *et al.*[15]

Since the absorptions due to U^{4+} in zircon vary greatly in intensity, it was necessary to use samples of different thicknesses and concentrations. Synthetic samples were made by the flux-growth method of Chase and Osmer[16] and contained ~0.1 wt% of U^{4+}.[17] Natural samples containing 0.02–0.4 wt% of U^{4+} (Ref. 17) were also studied. The natural samples had to be annealed for several hours at 1500 °C, just below the temperature at which zircon decomposes into zirconia and silica, to minimize broadening,[18,19] due to radiation damage,[20] of the U^{4+} absorptions. The optical samples were polished cuboids, a few millimeters in linear dimensions, with the c axes parallel to edges of the samples.

III. ABSORPTION MEASUREMENTS

The spectrum of U^{4+} in zircon, as reported by RKW, was confirmed over the 4000–30000-cm^{-1} range. The linewidths for synthetic samples lay in the 10–30-cm^{-1} range at liquid-helium temperatures. The corresponding linewidths in the annealed samples were (20–60)% greater. All the U^{4+} lines appeared to be intensity correlated in different samples, so that all the lines should be due to single-ion transitions. No lines attributable to U^{4+} were observed at energies below 4000 cm^{-1}, but any U^{4+} lines at energies below about 2000 cm^{-1} would be more or less masked by absorption due to silicate vibrations.[21]

IV. ZEEMAN SPECTRA

Neglecting for the moment the "hot" bands,[1] the strong σ lines are assumed to be zero-phonon transitions between doubly degenerate Γ_5 levels and singlet levels.[1,22] At 5 K, and with a magnetic field of 7.7 T applied parallel to the c axis, Zeeman splittings were observed in the axial spectrum and in the σ spectrum in transverse geometry. In particular, the strong σ line at 18610 cm^{-1} was clearly split into two components of equal intensity, while the strong σ line at 19382 cm^{-1}, which had the same zero-field width as the line at 18610 cm^{-1}, was not split or broadened. Thus the lines had different g values; so the ground state must be a singlet and the σ-polarized zero-phonon lines correspond to excited states with Γ_5 symmetry. The π lines would derive from singlet-singlet transitions, and, as expected, no Zeeman splittings were observed for the π spectrum. No effect on the σ or π spectra was observed when a magnetic field of 7.7 T was applied perpendicular to the c axis, as expected for f^2 in D_{2d} symmetry.

In a field of 20 T, applied parallel to the c axis, Zeeman splittings were observed for the strong σ lines at 16944, 18610, and 23104 cm^{-1}. The splittings for the 18610-cm^{-1} line in 7.7 and 20.5 T are shown in Fig. 1. No splittings were observed for the narrow "hot" lines at 17773 and 14474 cm^{-1}, which derive from a Γ_5 level, 155 cm^{-1} above the ground state.[1] No splittings were observed when a magnetic field of 20 T was applied perpendicular to the c axis, but shifts of order 20 cm^{-1} were noted. These line shifts were presumably of quadratic origin.

V. MCD SPECTRA

As expected for a singlet ground state, the strong σ lines gave the derivative A-type[23] MCD signals, the intensities of which were linear in magnetic field strength and temperature independent over the temperature range for which the profiles of the absorption peaks did not change appreciably. When the spectral resolution was reduced to about 30% of the half-width of the absorption line, the area under the signal appeared to approach an asymptotic value, although the MCD trace was still affected by the finite resolution at energies very near that of the absorption maximum. The MCD gave the signs of the g values, as well as the magnitudes. The magnitudes of the g values were derived from the zeroth moments of the absorption and modulus of the MCD signal (see Appendix). Many of the weak absorption features have A-type MCD, but, from this evidence alone, it could not be decided whether these weak features were of vibronic or electronic origin. Apart from an amp-

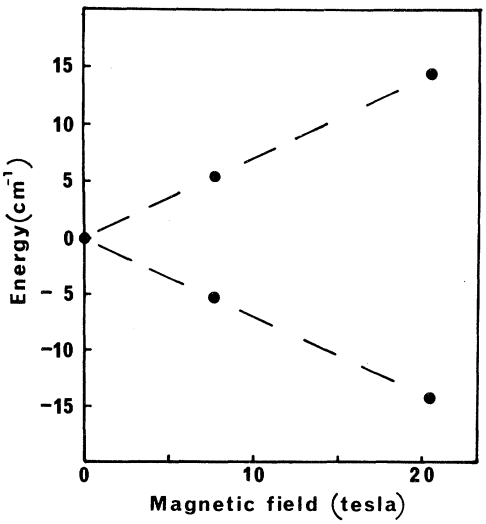

FIG. 1. Zeeman effect on 18610-cm^{-1} line. Splitting estimated to be accurate to ±2 cm^{-1}.

litude factor, the MCD spectra for synthetic and natural samples were identical. MCD and absorption spectra for natural samples are shown in Fig. 2, and the effect on the MCD of variations in spectral resolution is shown in Fig. 3.

VI. ASSIGNMENT OF LEVELS

The large number of strong lines in the π spectrum indicates that electronic lines of the π spectrum derive from $\Gamma_4 \rightarrow \Gamma_1$ transitions, with a Γ_4 being the ground state. There are 13 zero-phonon lines predicted in the range 4000–25000 cm^{-1} compared with 12 observed strong π lines. For any other singlet ground state, there would theoretically, be less than 12 zero-phonon lines in the same energy range.[1]

Although the selection rules give the number of zero-phonon σ lines, the intensity of some lines may be too low to observe experimentally. Actually, there are many more σ lines observed than there are theoretically predicted zero-phonon lines; so most of the weaker features are expected to be vibronic, as already mentioned. The absence of a common phonon sideband structure on the high-energy side of the strong lines is probably due to the ion-lattice coupling's being very dependent on the radial wave function of the U^{4+} ion, especially as the ionic radii of Zr^{4+} and U^{4+} differ appreciably (about 0.74 and 0.93 Å, respectively).

In the 5000–25000-cm^{-1} region there are 13 strong σ lines and a weak line at 13308 cm^{-1}, which has a large g value and lies more than 2000 cm^{-1} above the next strong σ line. The weak line at 13308 cm^{-1} appears, therefore, to be of electronic origin. There is also the Γ_5 level at 155 cm^{-1} (Ref. 1) and the energies of these 15 Γ_5 levels are given in Table I. Preliminary calculations for a large range of parameters indicated that there are three Γ_5 levels in the 0–5000-cm^{-1} range. For the f^2 configuration in D_{2d} symmetry, there are 21 Γ_5 states and hence four states are unaccounted for and the permutation of four states over 18 positions in the visible and near-infrared regions gives rise to a very large number of possible assignments.

Since crystal-field effects are likely to be so strong that an observed transition cannot be related to the free-ion term closest in energy, various guesses had to be made concerning the location of the "missing" transitions. Using a least-squares method and either random parameters or parameters based on a crystal-field lattice expansion,[24] very poor fits and a Γ_1 ground state were obtained. However, from these initial attempts it emerged that level 17 (the numbering of the Γ_5 levels in-

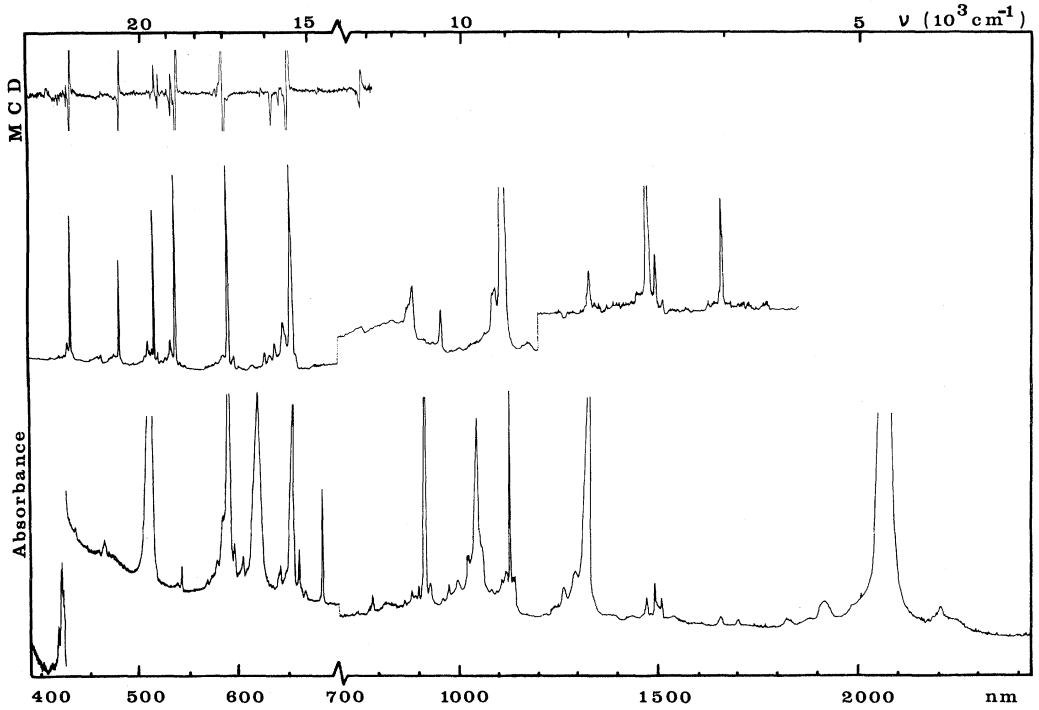

FIG. 2. Top: MCD spectrum at 15 K for 0.3-mm-thick zircon containing about 0.15-wt % U^{4+}. Magnetic field was 7.7 T and the resolution was about 15 cm^{-1}. Center: σ spectrum at 15 K for 1-mm-thick zircon containing about 0.25-wt % U^{4+}. Bottom: Corresponding π spectrum. Both π and σ spectra show weak lines (Ref. 17) due to U^{5+}.

creasing with increasing energy) always had a g value close to $+1.5$, and in most cases level 13 had a large positive g value. From the Zeeman data, the lines at 18610 and 13308 cm^{-1} were assigned to levels 17 and 13, respectively. The highest Γ_5 state was always calculated at about 23500 cm^{-1} with a g value of about $+1.5$, and hence the line at 23104 cm^{-1} was assigned as level 21. The lowest observed transition at 6033 cm^{-1} was assigned as level 4 (see above) and from Table I it can be seen that one state between 18610 and 23104 cm^{-1} is missing; one state between 13308 and 18610 cm^{-1} and two states in the 6033–13308-cm^{-1} range are also missing. These ranges are now discussed.

Zeeman experiments using the pulsed magnetic field of 20 T and the MCD indicated that observed lines at 18797, 18993, and 19268 cm^{-1} had g values of about $+1.5$ and hence could be assigned as phonon sidebands of the 18610-cm^{-1} transition. The line at 19382 cm^{-1} had a very small g value and the MCD spectrum showed virtually no evidence of the weak absorption lines in the 19382–19673-cm^{-1} range; hence these absorption lines were attributed to phonon sidebands of the 19382-cm^{-1} transition. No other features were observed in either absorption or MCD between 19673 cm^{-1} and the next strong absorption line at 20870 cm^{-1}. The missing level was therefore assumed to be between 20870 and 23104 cm^{-1} and the absorption and MCD spectra indicated it was the feature at 21645 cm^{-1}.

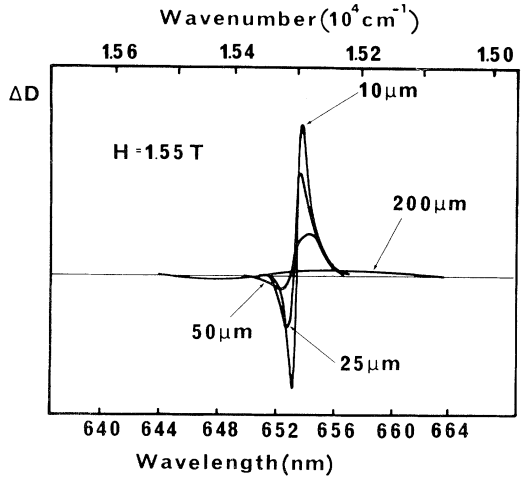

FIG. 3. Effect of spectral resolution for MCD signal derived from σ transition at 15303 cm^{-1}, which had a half-width of 30 cm^{-1}. Resolution = 0.8 cm^{-1} per micron of slit width. Data obtained at 15 K and in a magnetic field of 1.55 T. The results obtained with a slit width of 5 μm were nearly the same as those obtained with a slit width of 10 μm, except that the slope of ΔD near 15303 cm^{-1} was somewhat greater.

TABLE I. σ lines most likely to be due to zero-phonon transitions.

Energy (cm^{-1})	Energy (cm^{-1})	Energy (cm^{-1})
155	8966	16944
6033	10419	18610
6787	11232	19382
7528	13308	20870
8935	15303	23104

The missing Γ_5 level in the 13308–18610-cm^{-1} range is now considered. Both the MCD and absorption were virtually featureless between 13308 and 15303 cm^{-1} and between 16944 and 18644 cm^{-1}. In the 15303–16944-cm^{-1} region there were eight readily identifiable weak absorption lines, and, although no attempt was made at this stage to identify the missing Γ_5 level, the relative positions of levels 13–21 could be located.

In the 6033–7528-cm^{-1} range, no vibronic lines or extra transitions, apart from those due to U^{5+},[17] were observed, thus fixing levels 4, 5, and 6. The weak line at 8525 cm^{-1} was considered unlikely to be a phonon sideband of the 7528 cm^{-1} line and was assigned as level 7. The strong doublet at 8935 and 8966 cm^{-1} was assigned as levels 8 and 9, with the weaker doublet near 9150 cm^{-1} being attributed to phonon sidebands. Apart from the line at 10419 cm^{-1} (taken as level 10) no other structure was observed until the energy was increased to 11232 cm^{-1} (level 11). The last Γ_5 level was taken as the weak feature at 11913 cm^{-1}. This ordering of the levels is different from that used by RKW, and early at-

TABLE II. Parameters for zircon: U^{4+}.

	Point charge	RKW	Initial parameters	Best-fit parameters[a]
F_2		185.3	185.3	196.7±1.0
F_4		37.1	37.1	37.0±0.8
F_6		3.67	3.67	4.25±0.1
ζ		1780	1780	1740±7
α[b]			20	22.8±2.5
$A_2^0\langle r^2\rangle$	−6176	−349	−700	−1000±80
$A_4^0\langle r^4\rangle$	−9	400	450	250±50
$A_4^4\langle r^4\rangle$	4145	770	3750	5360±140[c]
$A_6^0\langle r^6\rangle$	−32	−435	−150	−362±16
$A_6^4\langle r^6\rangle$	−57	5.7	1800	−300±200[c]

[a]The "errors" in the best-fit parameters indicate the variations in the parameters required to increase the standard deviation of the fit by 4 cm^{-1}.

[b]α is the Trees (Ref. 25) correction.

[c]The signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ can be changed simultaneously without affecting the calculations.

TABLE III. Calculated and observed energy levels and g values for zircon: U^{4+}.

Energy[a] (cm^{-1})	Calculated Irreducible representation	g	Energy (cm^{-1})	Observed Irreducible representation	g
0	4				
281	5	−0.2	155	5	<0.2[f]
558	1				
1692	2				
1786	3				
1890	1				
2184	5				
4131	3				
4376	5				
4612	4		4736[b]	2,3,4	
4848	1		4853	1	
5721	3		5759[c]	3	
5915	5	0.7	6033	5	<0.4[f]
6039	2				
6692	4		6664[b]	2,3,4	
6766	5	−0.7	6787	5	<0.8[f]
7530	1		7557	1	
7535	2				
7648	5	2.9	7528	5	<0.4[f]
8546	4				
8608	5	−2.9	8525	5	e
8814	1		8894	1	
8820	3		8837[b]	2,3,4	
8894	5	−1.0	8935	5	−0.9
9038	2				
9164	5	1.1	8966	5	−0.5
9322	4				
9611	2				
9743	1		9594	1	
10160	3				
10477	5	−1.3	10419	5	−0.5
10957	1		10938	1	
11168	4				
11198	5	−0.8	11232	5	<0.3[f]
11589	3				
11794	4				
11886	5	−0.5	11913	5	e
12043	3				
12088	2				
12579	1		12755	1	
13267	5	4.5	13308	5	4.3
14549	1		14629	1	
15113	3		14918[b]	2,3,4	
15401	5	−0.4	15303	5	0.4
15468	1		15326	1	
15478	4		15254[b]	2,3,4	
15666	2				
15731	5	0.4	15723[d]	5	
16259	1		16117	1	
16266	4				
16763	1		16973	1	
16821	5	−0.8	16944	5	−0.9
17456	3				
17960	2		17928[b]	2,3,4	
18415	5	1.5	18610	5	1.5
19394	1		19522	1	
19471	5	−0.05	19382	5	<0.01[f]
19949	3				
20799	5	1.6	20870	5	0.6

TABLE III. Continued.

Energy[a] (cm^{-1})	Calculated Irreducible representation	g	Energy (cm^{-1})	Irreducible representation	g
20949	4				
20971	2				
21593	3				
21820	5	1.3	21645	5	~1
22046	1				
22276	4				
23041	5	1.5	23104	5	1.3
23202	3				
23740	1		23718	1	
24462	4				
42191	1				

[a]Calculated using parameters in Table III.
[b]Levels based on transitions from Γ_5 state at 155 cm^{-1}.
[c]Magnetic dipole transition.
[d]Γ_5 level not used in fitting procedure.
[e]Absorption intensity too low to obtain Zeeman result.
[f]Where upper limits to g values are given, the sign of the g value is unknown.

tempts to fit the spectrum, using their assignments, proved fruitless.

The crystal-field splitting of the $^3H_4$ term was examined to suggest an initial set of parameters. [The free-ion designations $^3H_4$, $^3P_2$, and $^3P_1$ are only approximate descriptions, as the wave functions are mixed.] The aim was to obtain a Γ_4 ground state, a Γ_5 state at about 155 cm^{-1}, with $|g| < 0.2$, and all other states at energies greater than 300 cm^{-1} [since only one set of "hot" bands was observed experimentally at temperatures up to 300 K (Ref. 1)]. These conditions could be produced with a fairly wide range of parameters; so an additional constraint was imposed, viz., that the $^3P_2(\Gamma_1, \Gamma_5)$ splitting should be 614 cm^{-1}. The complete 91×91 matrix had to be diagonalized, as a first-order calculation proved inadequate. The g values of the $^3P_2(\Gamma_5)$ and $^3P_1(\Gamma_5)$ states were found to be fairly close to the experimental values. The g value was defined to be positive when the Γ_5 state characterized by $\sum_i a_i |\text{LSJM}; M = 5, 1 \text{ or } -3\rangle$ was calculated to be the higher-energy level in the presence of an axial magnetic field. The g values as defined are subject to the sum rule $\sum_i g_i = 6.0$. The RKW value of the spin-orbit parameter $\zeta = 1780$ cm^{-1} yielded a satisfactory $^3P_2(\Gamma_5) - {}^3P_1(\Gamma_5)$ splitting. The initial crystal-field parameters derived from these calculations are given in Table II.

VII. FITTING OF THE SPECTRUM

For actinide ions, the large crystal field and spin-orbit interactions cause much scrambling of the middle levels in a configuration and tend to produce an approximately uniform level spacing. It is easy therefore to obtain "false" minima in least-squares fitting routines as wide parameter variations may produce only relatively small changes in the energy levels. The observation of g values provides in principle a check since the g values depend on wave functions rather than energies.

The first stage of the fitting procedure was to fit the σ spectrum by least squares. A 21×21 matrix was diagonalized and led ultimately to a fit which had a standard deviation of 80 cm^{-1} with respect to the observed levels. However, the resultant parameters gave a much poorer fit (a standard deviation of 300 cm^{-1}) for the π spectrum. The overall fit was improved by variation of the parameters, either singly or in linear combinations, which appeared likely to lower the deviations for levels which exhibited the greatest misfits. For this purpose derivatives of the line positions with respect to the parameters were obtained. The convergence of the results indicated that a minimum of the standard deviation had been reached within a few cm^{-1}. The standard deviation for 30 levels was reduced to 112 cm^{-1} with standard deviations of 107 and 118 cm^{-1} for 18 σ and 12 π levels, respectively. The parameters are given in Table II and energy levels and g values in Table III. The missing Γ_5 state (level 15), calculated to be at 15731 cm^{-1}, with a g value of +0.4, could well correspond to a fairly weak transition observed in absorption at 15723 ± 10 cm^{-1}, which gave a fairly strong B-type[23] MCD signal with a negligible A-type component ($g \leq 0.1$). The magnetic dipole transition observed[1] at 5739 cm^{-1} is allowed only for a $\Gamma_4 \rightarrow \Gamma_3$ transition according to selection rules[1] and on this basis is assigned to the

Γ_3 level calculated at 5721 cm^{-1}.

The fit for the g values was good for the majority of cases, but there were substantial discrepancies in the calculated and observed values for levels 6, 9, and 19. The calculated g values for levels 8, 9, and 10 were rather sensitive to the choice of parameters. However, for level 6, where the greatest discrepancy between calculation and experiment was observed, the g value did not seem to be very sensitive to the choice of parameters.

The final parameters are given in Table II, together with the starting parameters, the RKW parameters, and the values obtained from a point-charge model. The latter calculation was performed[24] over a sphere of radius 6 Å, assuming point charges of +4, +4, and −2 for Zr, Si, and O, respectively, and assuming the radial integrals of Lenander.[26] The point-charge model failed to produce a reasonable fit of the spectrum; this failure was expected because of the large ionic charges, the rather small number of shells used, and covalent effects which would be particularly important within the SiO_4^{4-} tetrahedra. As mentioned by RKW, the signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ may be changed simultaneously without affecting the energies or g values. The calculated and observed spectra are shown in Fig. 4.

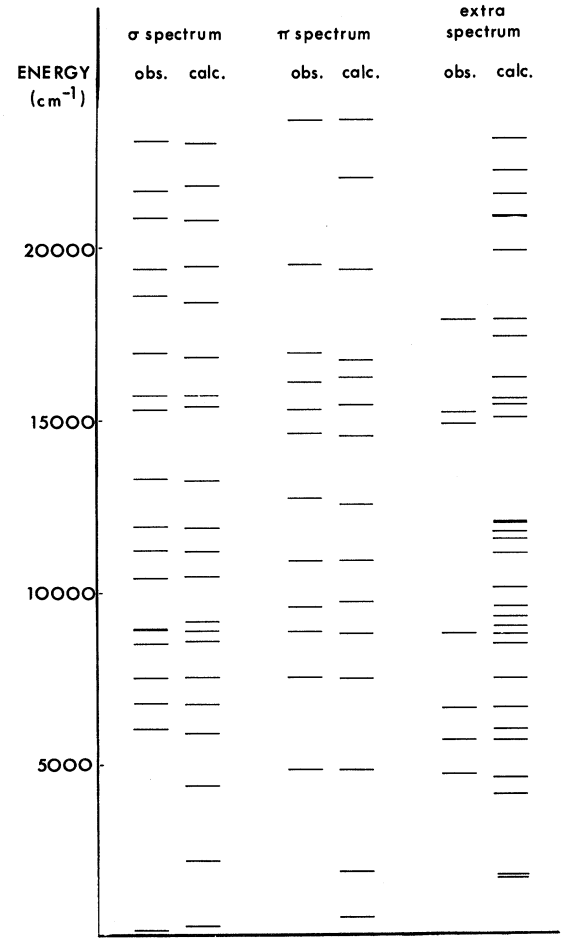

FIG. 4. Diagrammatic representation of calculated and observed zero-phonon transitions for zircon: U^{4+}.

As far as the energy levels are concerned, the fit obtained in the present work is comparable to that of Satten *et al.*[7], who fitted 18 levels for Cs_2UCl_6 (U^{4+} was regarded as being in octahedral symmetry as it was argued that the trigonal part of the crystal field was negligible) with a standard deviation of 126 cm^{-1} and that of Gruber and Hecht,[27] who fitted 23 levels for gaseous UCl_4 (tetrahedral symmetry) with a standard deviation of 74 cm^{-1}. Hecht and Gruber[28] have extended their analysis to single-crystal UCl_4, symmetry D_{2d}. Our program confirmed their calculated energy levels to 1 cm^{-1}, and hence it is all the more surprising that they claim to reproduce the calculations of RKW. Even the RKW results for zero crystal field are found by us to contain errors of about 60 cm^{-1}.

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APPENDIX: CALCULATION OF g VALUES FROM A-TERM (DERIVATIVE) MCD SIGNALS

It is assumed that the ground state is a singlet and that the excited state is an orbital doublet, with magnetic quantum numbers $M_J = \pm 1$. The MCD signal $\Delta D(\nu)$ is given by $2g\mu_B H D'(\nu)$, where $D(\nu)$ is the absorption and $D'(\nu)$ is the derivative of the absorption with respect to energy. However, in the present work the absorption lines were fairly narrow, and g values could not be found by matching the amplitudes of the derivatives of the absorption lines with the MCD signals, because of finite resolution effects.

For nonoverlapping bands, the MCD can be analyzed using the first and second moments of the MCD signals.[23,29] However, in the present case, the bands were often close to each other, and uncertainties in the wings of the bands lead to errors which increase with n, where n refers to the n^{th} moment. Thus the zeroth moments of the moduli of the MCD signals were used.

For a Lorentzian line shape, $D(\nu) = D_m/(1+x^2)$, where $x = (\nu - \nu_0)/\gamma$ and γ is half the linewidth at half-height, $D(\nu) = D_+ - D_- = 2g\mu_B H D_m x/\gamma(1+x^2)^2$

(see Boccara *et al.*[30]), and it is easily found, assuming fairly narrow lines, that $|g| = K\gamma \langle |\Delta D| \rangle_0 / \mu_B H \langle D \rangle_0$, the sign being given by the slope of $D(\nu)$ at $\nu = \nu_0$. For a Lorentzian, $K = 1.57$, and, following a similar method of analysis, $K = 1.06$ and 1.22 for a Gaussian and the square of a Lorentzian, respectively. In the calculations for zircon: U^{4+}, K was taken as 1.2, intermediate between values appropriate to a Gaussian and a Lorentzian. For lines which gave g values directly from Zeeman experiments, the g values obtained from the MCD traces agreed within 20% of those obtained directly The errors appeared to lie in line-shape variations. In cases where no Zeeman splitting could be observed, the errors in the evaluation of the zeroth moments of the MCD and absorption were small and the errors of the g values in these cases are probably (20–30)%. However, both the absorption and MCD of the line at 21645 cm^{-1} were very weak and the g value is accordingly very approximate.

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