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Optical spectra of U^{4+} and U^{5+} in zircon, hafnon, and thorite

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The optical spectra of U^{4+} and U^{5+} doped into hafnon ($HfSiO_4$) and thorite ($ThSiO_4$) are reported. However, no significant information was obtained on the validity of a previous crystal-field fit of the absorption spectrum of U^{4+} doped into zircon ($ZrSiO_4$). New experiments confirm the interpretation of Judd and Runciman of the Zeeman behavior of zircon:U^{5+}.

I. INTRODUCTION

The low-temperature polarized optical spectra of U^{4+} in zircon have been reported by Richman *et al.*[1] who also calculated crystal-field parameters from their data. Mackey *et al.*[2] found that the calculations of Richman *et al.* were incorrect and put forward an alternative set of crystal-field parameters, together with some Zeeman data. Although the agreement between the experimental and calculated (least-squares best-fit) energy levels was generally very good, there were a number of discrepancies between the calculated and experimental g values. It was also found possible to change some of the crystal-field and interelectron repulsion parameters by quite large amounts and yet produce only minor changes in the overall standard deviation of the discrepancy between the calculated and experimental values. Hence there is a possibility that the parameters for zircon:U^{4+} are not unique and the present study was undertaken to find whether similar parameters could reproduce the absorption spectra of U^{4+} in the isomorphous lattices of hafnon and thorite.

In previous studies of U^{5+} doped into zircon[3,4] we proposed that the angular dependence of the Zeeman spectra of the 9026-cm^{-1} line showed that there was an accidental degeneracy in the ground state. However, Judd and Runciman[5] have explained the Zeeman behavior without invoking an accidental degeneracy and a further aim of the present work was to perform a more detailed Zeeman study. We also report the spectra of U^{5+} in hafnon and thorite.

II. EXPERIMENTAL

The optical and Zeeman studies were carried out as described previously.[2,4] The least-squares fitting of the crystal field, interelectron repulsion, and spin-orbit coupling was performed on the σ spectrum only, and then the π spectrum was calculated for comparison with the experimental spectrum.

The hafnon crystals were grown the same way as for the zircons of Chase and Osmer[6]; the thorites were also grown as described by Chase and Osmer[6] and the maximum concentration of uranium in the crystals was found to be approximately 0.1% by weight. As for zircon,[3] the uranium tended toward the tetravalent state when only UO_2 was added to the starting material; U^{5+} was preferred when both UO_2 and Y_2O_3 were added.

The largest inclusion-free hafnons were about 2 mm on each side, while the best thorites were needle-like with the c axis lying along the long dimension and were terminated by (101) faces. These crystals were up to 15 mm long and 1–2 mm wide. Thorites doped with appreciable amounts of either U^{4+} or U^{5+} were pale green, the color being unaffected by prolonged annealing in air at temperatures up to 1300 °C. All these thorites exhibited striations parallel to the c axis and it was extremely difficult to cut the crystals perpendicular to the c axis without fracture. The largest thin sample which could be cut for magnetic circular dichroism (MCD) and axial Zeeman studies was only approximately 0.5 mm^2 in area and about 0.4 mm thick.

As mentioned previously,[4] it was difficult to measure the Zeeman spectra of the U^{5+} lines in synthetic crystals because of their small size and because the lines were in the infrared. Thus a relatively large natural zircon was used. The zircon, from Thailand, was $6 \times 7 \times 1$ mm and had its large faces cut perpendicular to the c axis. After prolonged annealing in air at 1300 °C, the half-widths of the 9026- and 6700-cm^{-1} lines were 6 and 2 cm^{-1}, respectively. These values are only slightly larger than those in synthetic zircons containing approximately 0.01-wt% U^{5+}. In zero magnetic field, the peak absorbances of both lines were about unity at low temperatures.

III. RESULTS AND DISCUSSION

A. U^{4+} absorption spectra

Since there is little change in lattice parameters on replacing Zr^{4+} by Hf^{4+},[7] it is not surprising that

TABLE I. Observed and calculated energies of Γ_5 levels (cm^{-1}) for U^{4+} doped into zircon, hafnon, and thorite. The observed levels (above level 3) were derived from the σ spectra.

					Thorite		
	Zircon		Hafnon		Set 1		Set 2 [a]
Level	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	281	155	191	147	157	220	234
2	2 184		2 358		2 179		2 095
3	4 376		4 290		3 972		4 176
4	5 915	6 033	5 951	6 044	5 837	5 950	5 913
5	6 766	6 787	6 771	6 810	6 495		6 644
6	7 648	7 528	7 711		7 307		7 491
7	8 608	8 525	8 677		8 345		8 554
8	8 894	8 935	8 978	8 942	8 634	8 730	8 677
9	9 164	8 966	9 002	8 977	8 801	8 810	8 855
10	10 477	10 419	10 530	10 471	10 153	9 850	10 181
11	11 198	11 232	11 278	11 274	11 098	10 990	11 111
12	11 886	11 913	11 981		11 739		11 877
13	13 267	13 308	13 418		13 158		13 246
14	15 401	15 303	15 431	15 347	15 006	15 065	15 024
15	15 731	15 723	15 811		15 636	15 685	15 572
16	16 821	16 944	16 931	16 989	16 483	16 500	16 534
17	18 415	18 610	18 697	18 688	18 087	18 116	18 144
18	19 471	19 382	19 362	19 383	19 669	19 840	19 603
19	20 799	20 870	20 772	20 820	20 708	20 550	20 654
20	21 820	21 645	21 644		21 515		21 698
21	23 041	23 104	23 182	23 180	22 789	22 730	22 923

[a] For parameter set 2, the lines observed at 8730 and 8810 cm^{-1} were assumed to be due to transitions to levels 7 and 8, respectively.

the absorption spectrum of U^{4+} in hafnon is very similar to that in zircon. The relative intensities of the absorption peaks were almost the same in both materials and the energy shifts were a few tens of cm^{-1} (Tables I and II). However, Th^{4+} is considerably larger than Zr^{4+} and the optical spectrum of U^{4+} in thorite is considerably different from that in zircon. The spectrum is shown in Fig. 1. Relative to zircon: U^{4+}, the σ-polarized transitions were shifted a few hundred cm^{-1} and the rela-

TABLE II. Observed and calculated energies of Γ_1 levels (cm^{-1}) for U^{4+} doped into zircon, hafnon, and thorite. The observed levels were derived from the π spectra.

					Thorite		
	Zircon		Hafnon		Set 1		Set 2
Level	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	558		403		270		372
2	1 890		1 850		1427		1 582
3	4 848	4 853	4 969	4 878	4 781		4 770
4	7 530	7 557	7 730	7 642	7 491		7 430
5	8 814	8 894	8 529	8 897	8 102	8 330	8 298
6	9 743	9 594	9 843	9 872	9 381		9 404
7	10 957	10 938	10 847	10 947	10 703	10 929	10 921
8	12 580	12 755	12 602		12 259		12 381
9	14 549	14 629	14 325	14 635	13 862	14 745	14 121
10	15 469	15 326	15 371	15 335	15 019	15 354	15 150
11	16 259	16 117	16 438	16 142	15 822	15 681	16 018
12	16 763	16 973	16 817	17 027	16 620	16 611	16 490
13	19 394	19 522	19 489	19 531	19 750	19 833	19 532
14	22 046	21 550	21 897		21 820		21 912
15	23 740	23 718	24 162	23 753	24 001	23 084	23 813
16	42 191		42 265		42 888		41 125

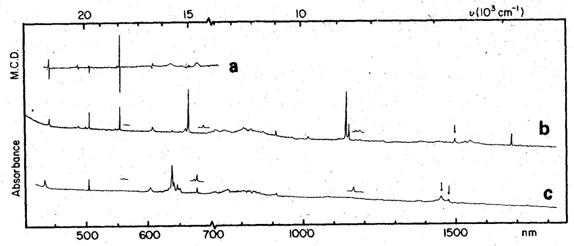

FIG. 1. (a) MCD spectrum of ThSiO$_4$:U^{4+} at approximately 10 K and a magnetic field of 7.5 T applied along the *c* axis. (b) σ spectrum of ThSiO$_4$:U^{4+} at approximately 10 K. The broad features between 700 and 900 nm are of instrumental origin. The line marked by an arrow is due to U^{5+}. The small spectral sections above the main low-temperature spectrum show the "hot" lines observed at 135 K. (c) π-spectrum of ThSiO$_4$:U^{4+} at approximately 10 K. The same comments apply as for the σ spectrum. The small spectral section near 15 000 cm^{-1}, above the main spectrum shows the enhancement of the zero-phonon 14 745-cm^{-1} line on heating to 135 K.

tive intensities of the peaks were markedly altered. However, the change in the π spectrum was even more pronounced, the most obvious difference being the general weakness of the peaks apart from those in the 14 000–17 000-cm^{-1} region. At high resolution, it was evident that the absorption peaks were asymmetric or partly split even though the Laue spots in back-reflection x-ray photographs were quite sharp, indicating a lack of gross straining or twinning. Annealing failed to sharpen the optical absorption lines and it may be that the broadening and splitting are due to concentration effects rather than random strains in the crystals.

From spectral measurements as a function of temperature, the first observable excited state is located at 147 ± 5 and 220 ± 10 cm^{-1} in hafnon:U^{4+} and thorite:U^{4+}, respectively, compared with 155 cm^{-1} in zircon:U^{4+}.[1] As in zircon:U^{4+} (with the exception of the weak line at 5759 cm^{-1}), the observed axial and σ spectra of hafnon:U^{4+} and thorite:U^{4+} were identical showing the transitions to be electric dipole allowed. The MCD spectra (see later) show the ground state to be a singlet and the selection rules for the "hot" lines in hafnon:U^{4+} and thorite:U^{4+} imply that the low-lying excited state is a Γ_5 (using the notation of Koster *et al.*[8]) doublet in both cases. We assume that the U^{4+} ground state is a Γ_4 state in all cases[2] so that the low-temperature σ and π spectra are due to $\Gamma_4 \rightarrow \Gamma_5$ and $\Gamma_4 \rightarrow \Gamma_1$ transitions, respectively. In all our synthetic samples, the numbers of σ and π levels were less than those predicted (21 and 16, respectively) so that without a prior assignment of the zircon:U^{4+} spectrum, it would not be feasible to attempt even to assign the relative order of the energy levels of U^{4+} in our crystals of thorite and hafnon.

However, as mentioned above, the lines in the hafnon:U^{4+} spectrum are generally within 50 cm^{-1} of their counterparts in zircon:U^{4+} and hence, given the correctness of the zircon:U^{4+} assignment,[2] the hafnon:U^{4+} assignment is obvious. This is not the case for thorite:U^{4+} where the shifts are large compared with zircon:U^{4+} (see below).

Since the shifts of the hafnon:U^{4+} levels relative to zircon:U^{4+} were less than the standard deviation of the overall fit for the zircon:U^{4+} spectrum,[2] no serious fitting was performed for the hafnon:U^{4+} spectrum, although using the calculated parameters for zircon:U^{4+} as a basis for fitting the hafnon:U^{4+} spectrum, a fit with a standard deviation of 125 cm^{-1} was obtained compared with 112 cm^{-1} for zircon:U^{4+} (Ref. 2). The problems that can be encountered when fitting a limited number of levels are readily demonstrated by a least-squares fit for hafnon:U^{4+} using only the Γ_5 states in the order given in Table I. The values of F_2, F_4, F_6, ζ, and α were kept the same as for the zircon:U^{4+} fit[2] on the basis that small changes in ionic radii when replacing Zr^{4+} by Hf^{4+} would produce mainly effects on the crystal-field parameters. With this restriction, the Γ_5 levels can be fitted with a standard deviation of 49 cm^{-1} using the parameters shown in Table III. However, the standard deviation of the π spectrum was 225 cm^{-1}.

Due to the large shifts in transition energies of thorite:U^{4+} relative to zircon:U^{4+} (Table I), there are greater problems associated with fitting the small number of Γ_5 levels in the former compound since it is no longer possible to find an unambiguous correlation between energy levels. The Γ_5 states above 15 000 cm^{-1} can be assigned as levels 14 to 21 inclusive (see Ref. 2 for a discussion of the ordering of the 21 allowed $\Gamma_4 \rightarrow \Gamma_5$ transitions) with level 20 missing (this transition is very

TABLE III. Parameters used in crystal-field calculations (cm^{-1}).

	Zircon	Hafnon	Thorite	
			Set 1	Set 2
F_2	196.7	196.7	205.9	203.2
F_4	37.0	37.0	34.5	30.8
F_6	4.25	4.25	4.79	4.27
ζ	1740	1740	1711	1735
α	22.8	22.8	25.0	27.3
$A_2^0\langle r^2\rangle$	−1000	−1398	−1058	−790
$A_4^0\langle r^4\rangle$	250	458	542	353
$A_4^4\langle r^4\rangle$	−5360	−5019	−4570	−5215
$A_6^0\langle r^6\rangle$	−362	−346	−373	−384
$A_6^4\langle r^6\rangle$	300	150	118	298

TABLE IV. Observed and calculated g values for high-lying Γ_5 states of thorite:U^{4+}. The parameters used in the calculations are given in Table III.

Level	Observed	Calculated	
		Set 1	Set 2
14	+ve[a]	0.20	−0.07
15	−ve[a]	−0.09	−0.53
16	−1.4	−1.09	−0.22
17	1.5	1.60	1.56
18	0.3[b]	−0.54	−0.21
19	3.2	2.41	2.43
20	...	0.99	0.68
21	1.9	1.45	1.38

[a] Transitions too weak to estimate magnitude.

[b] Large B term present.

weak in zircon:U^{4+}) and this assignment is in agreement with the Zeeman data (see later). However, five of the expected transitions between 4000 and 15 000 cm^{-1} are not observed and there are a very large number of ways of ordering the five observed levels in this energy range. Two possible assignments are given in Table I, but the standard deviations of the fits to the σ spectra are 124 and 153 cm^{-1} for parameter sets 1 and 2, respectively. These results bear comparison with hafnon:U^{4+} where the same number of transitions in the σ spectrum can be fitted with a standard deviation of 49 cm^{-1} (see above). The disparity between the resultant calculated π spectrum and the experimental π spectrum is even more marked and level 15 is calculated to be approximately 1000 cm^{-1} too high for both sets of parameters.

It seems highly probable that neither assignment for thorite:U^{4+} is correct and, in order to obtain meaningful results, more transitions need to be located in more concentrated and/or thicker crystals.

B. Zeeman studies of thorite:U^{4+}

The MCD spectrum of thorite:U^{4+} is shown in Fig. 1 and consists almost entirely of temperature-independent derivative signals as expected for a singlet ground state. Quantitative interpretation of the MCD spectrum is complicated by two factors: (i) because of the small sample size the spectrum shown in Fig. 1 is not completely resolved (resolution approximately 5 Å) and (ii) as mentioned earlier, the absorption lines showed structure. In this sample, the 18 116-cm^{-1} line was split by approximately 7 cm^{-1} in zero field. However, the linewidth increased considerably in an axial magnetic field of 7.5 T and the broadening was consistent with an excited-state g value of approximately 1.5. For a wide range of parameters, level 17 in the σ spectrum consists largely of the $^3P_1$ term and is calculated to have a g value of approximately 1.5. This result is analogous to our previous[2] measurements on the 18 610-cm^{-1} line in zircon:U^{4+}. If we assume level 17 to lie at 18 116 cm^{-1} and that level 20 is not observed (the transition is very weak in zircon:U^{4+}), then the assignment of levels 14 to 21 is straightforward.

There is rough agreement between the calculated and experimental g values although the "experimental" g values are only approximate because of the previously mentioned complications. The "experimental" g values were determined by taking the ratios of the peak heights of the MCD and absorption spectra and normalizing to 1.5 for the 18 116-cm^{-1} line. These g values are probably only accurate to a factor of 2. The MCD results clearly favor parameter set 1, but, as discussed before, this parameter set is not believed to be reliable.

The broad weak-temperature-dependent features near 15 000 cm^{-1} are not considered to be related to the U^{4+} lines and may be due to color centers or impurities.

C. U^{5+} spectra

The main interest in the Zeeman spectra of zircon:U^{5+} was to experimentally distinguish between the interpretations of Vance and Mackey[4] and that of Judd and Runciman.[5] The angular dependence of the polarized transverse Zeeman spectra of the 9026-cm^{-1} line was studied with adequate resolution by Vance and Mackey, but the line was too broad to distinguish between the two interpretations unless a detailed line shape analysis was performed or magnetic fields of approximately 10 T were used. Although the 6700-cm^{-1} line was sufficiently narrow, we were not able to obtain adequate resolution in our previous measurements.

In this work, the 6700-cm^{-1} line was studied using a spectral resolution of 1 cm^{-1} (the half-width of the line was 2 cm^{-1}) as against approximately 4 cm^{-1} previously.[4] With the light propagating along $\langle 001 \rangle$ and with the magnetic field H (perpendicular to $\langle 001 \rangle$) along a twofold axis, different two-line patterns were observed for $\vec{E} \parallel \vec{H}$ and $\vec{E} \perp \vec{H}$; with H lying in a direction other than along a twofold axis, a four-line pattern was observed in both the $\vec{E} \parallel \vec{H}$ and $\vec{E} \perp \vec{H}$ polarizations, there being, of course, a difference in the line intensities except when H lay midway between a $\langle 100 \rangle$ and a $\langle 110 \rangle$ direction. It was clear that the angular dependence of the Zeeman patterns reflected variations in intensity not energy.

The results were therefore in accord with the predictions of Judd and Runciman[5] and show that the

TABLE V. Best estimates of g values for zircon:U^{5+}.

Energy level (cm^{-1})	$g_{\parallel}$	$g_{\perp}$
9026	1.2	2.3
6700	0.8	2.7
0	~0.2	0.6

6700-cm^{-1} transition is of the $\Gamma_6 \rightarrow \Gamma_6$ or the $\Gamma_7 \rightarrow \Gamma_7$ type. In a magnetic field of 5 T, the ground-state splitting was deduced to be 1.6 ± 0.2 cm^{-1} in agreement with the value derived previously for the 9026-cm^{-1} line (see Fig. 3 of Ref. 4). [Note that in the last sentence of the caption of Fig. 3 (Ref. 4), "⟨100⟩" should be replaced by "⟨001⟩."] Our best estimates of the g values for the ground state and the 6700- and 9026-cm^{-1} levels for zircon:U^{5+} are given in Table V. There is still poor agreement between these revised values and those calculated previously.[4]

For U^{5+} in hafnon, the corresponding lines were observed at 6702 and 9079 cm^{-1}, and for U^{5+} in thorite only one sharp σ line was observed at 6700 cm^{-1}. The temperature dependence of the intensities were very similar to those found for zircon:U^{5+} (Ref. 4), and we still have no adequate explanation of this effect. The behavior of the 14 745-cm^{-1} line in the π spectrum of thorite:U^{4+} is similar except that the intensity increase with temperature is more gradual.

IV. CONCLUSIONS AND FINAL REMARKS

We have obtained spectral data on the systems hafnon:U^{4+}, U^{5+} and thorite:U^{4+}, U^{5+}. However, the U^{4+} spectra gave no further information on the uniqueness or otherwise of the previous zircon:U^{4+} fit.[2] For hafnon:U^{4+} the shifts of the energy levels on replacing Zr^{4+} by Hf^{4+} were less than the standard deviation of the fit of the zircon:U^{4+} spectrum. For thorite:U^{4+}, insufficient levels were observed, especially in the π spectrum, to obtain a meaningful set of parameters within the crystal-field model.

It is appropriate to mention here that Richman *et al.*[1] were incorrect in stating that the signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ can be simultaneously interchanged without any effect. Although the energies and g values are unaffected, the Γ_3 and Γ_4 states are interchanged. The number of π lines in the zircon:U^{4+} spectrum was taken as evidence by Mackey *et al.*[2] that the ground state is of Γ_4 symmetry. However, the signs of $A_4^4\langle r^4\rangle$ and $A_6^4\langle r^6\rangle$ given by them are incorrect.

For U^{5+} in zircon, the present Zeeman results make it clear that the theory of Judd and Runciman[5] is correct and that there is no accidental degeneracy in the ground state as suggested previously.[4]

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