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Publication Date
1963-11-07

UCRL-11099

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Submitted to Journal of Chemical Physics

UCRL-11099

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AEC Contract No. W-7405-eng-48

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ABSTRACT

It has been possible to assign the ten lowest energy levels of AmIV. By using these assignments and the complete spin orbit matrices, a fit was obtained with 5f hydrogenic wave functions. This fit was then improved by using a fitting program and varying all four parameters. Comparison calculations using hydrogenic wave functions are made for PuI. For AmIV the hydrogenic values are $F_2 = 268.6\ cm^{-1}$ and $\zeta = 2605\ cm^{-1}$; the corresponding values for PuI are $F_2 = 230.6\ cm^{-1}$ and $\zeta = 2174.6\ cm^{-1}$.

INTRODUCTION

To date an analysis of the solid-state spectrum of AmIV (3+ ion) has not been possible with the available absorption and fluorescence data. This is due to several reasons; one is that with a ground state of J = 0 and crystal symmetry of C_{3h} it is difficult to determine the J values.[1] A second difficulty is that in the actinide elements the LS coupling scheme is not followed and therefore one must perform rather detailed calculations in the intermediate coupling scheme before much of a guide to the spectrum can be obtained.[2]

The complete spin orbit matrices have now been calculated by G. F. Koster and C. W. Nielson;[3] earlier incomplete matrices of Ofelt were useful.[4]

There is some question as to the assignments made by Gruber[5] to the various infrared absorption peaks. A comparison between PuI and AmIV (both $5f^6$) did not give as close an agreement as might be expected.[6] Furthermore the selection rule of Ofelt indicates that Gruber should not have seen transitions between J = 0 and J = 3 or 5.[7] The J = 0 to J = 1 is a magnetic dipole transition and is expected to be weak.

This work was undertaken in an attempt to better understand some of these discrepancies and if possible assign some of the upper levels of AmIV.

The method chosen to study the low levels of AmIV was that of "selective excitation," where narrow band widths of light are used to excite fluorescence to low levels.[8] Near-infrared absorption experiments are used to obtain the higher levels of the ground multiplet.

EXPERIMENTAL

For the selective-excitation experiments a 1000-W Hg arc (AH6) was mounted in the source compartment of a Beckman DU monochromator with the output incident on the americium crystal mounted in a quartz dewar filled with liquid nitrogen. The crystal was imaged on the slit of a f/6.3 spectrograph.

Exposures from one-half hour to several days were taken throughout the photographic range. The crystal is the same one used by Gruber and Conway.[9]

The fluorescence emitted by the crystal brightens as the wavelength of the exciting light coincides with the absorption peaks of the americium ion. There is a self-luminescence to the crystal which is excited by the energy of the radioactive decay. Any spectrum, is, therefore, a mixture of both the selectively excited and self-luminescence emissions.

Wavelengths of 510, 410, and 368 mμ produced the brightest emissions and were therefore investigated first. The spectrum obtained upon irradiating with 510 mμ light is relatively simple, showing only three groups of lines. There are no absorption peaks in the region 5100 to 8000 Å.

When 410-mμ light is used, many new emissions appear in addition to the groups excited by the 510-mμ light. The 510 groups are now weaker. A strong line appears at 4623 Å where there is also a narrow absorption peak of the americium ion. Later experiments using 462-mμ light revealed that the intense emissions attributed to 410 actually come from the 4623-Å level. When 368-mμ light is used many new emissions appear but the previously observed groups also appear.

It appears that at the lowest energy all that happens is that transitions to the levels of the ground multiplet take place. But as the incident energy is increased it is possible to get emission to ground from this particular level and also a transfer of energy to the lower levels with emission to ground. This transfer of energy between upper levels and the accompanying emission greatly complicates the problem. The nature of the transfer between upper levels is not known. If the transfer is by radiation the lines would appear in the infrared beyond the region studied.

This exchange of energy also indicates that there would be little hope of analyzing the usual fluorescence data which is obtained by irradiation with wide-wavelength regions of ultraviolet light.

Table I presents the results of the selective-excitation experiments. The only new absorption data is for J = 5. Two very weak lines are observed at 9258 and 9135 Å. This agrees with the very weak peaks seen by Carnall and Fields in the molten-salt solution of $Am(NO_3)_3$ in Li-K nitrate eutectic.[10] The position of these lines does not permit an accurate location of the J = 5 level since they are only two of four possible lines and there are a total of seven possible levels. Table II lists the data above 8000 Å that was used. Except for J = 5 the data are due to Gruber.[5]

RESULTS

An analysis of the data in Tables I and II makes possible the assignments for the ^7F multiplet listed in Table III. The calculations were made by using the spin orbit matrices of Koster and Nielson.[3] The calculations were made with 5f hydrogenic wave functions and were carried out using the form E/F_2 instead of energy, and $\chi(=\zeta/F_2)$ instead of ζ. In this form the results are more easily applied to other $5f^6$ cases. Figure 1 is a plot of these results between χ of 9 and 10. It is possible on a plot of this nature to incorporate the data for PuI and AmIV. These calculations for PuI are an improvement over the previously published values since the matrices now included singlets. Table III included the calculations for energy and g value for PuI. The calculations for AmIV are for values $F_2 = 268\ cm^{-1}$ and $\zeta = 2605\ cm^{-1}$; the PuI values are $F_2 = 230.6\ cm^{-1}$ and $\zeta = 2174.6\ cm^{-1}$.

Once the fit to hydrogenic values was obtained it was decided to vary the wave-function parameters and to see if it would be possible to obtain a new wave function that would better define the data. Now instead of only two variables

there are four variables. A Variable Metric Minimization Program known as Virment was used. (These calculations were done by T. P. Clements of the Lawrence Radiation Laboratory Mathematics and Computing Group.) The program in effect tries to minimize the sum of the squares of the difference between the observed and calculated values. The ground state is not fixed but can also vary. It has not been possible to carry these calculations to the completeness that the program is capable of, because of the great amount of computer time needed. It has been carried far enough to know that the parameters are not going to change by more than 1% of these values in going to completion. The J = 5 was not used in this fitting process. Table III also gives the fitted values. The fitted wave function is not much different from the hydrogenic.

The line at 21916 cm^{-1} has a g value of 0.72.[8] A calculation of the g value of the $^5G_2$ level using 5f hydrogenic wave functions is 0.65. The g value calculated for $^5D_2$ is 1.42; however, the line at 21624 cm^{-1} is a very broad line and the line was observed to broaden in a magnetic field, but no measurement was possible.

Before undertaking a study of the crystal-field parameters more accurate measurements will be attempted on both the absorption and fluorescence.

ACKNOWLEDGMENTS

I wish to thank Miss Mary Buchley of the Vallejo Junior College (Vallejo, California) for her help with the selective excitation experiments, and T. P. Clements for the help with the fitting program.

FOOTNOTE AND REFERENCES

† Work done under the auspices of the U. S. Atomic Energy Commission.

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Table I. Wavelengths of fluorescence lines excited by different energies.

Wave number (cm^{-1})	Wavelength (Å)	Notes	Wavelength of exciting light (mμ)[a] 510	462[b]	368[b]	Assignment
11842	8441		7687	Same as 510		$^5L_6$-$^7F_3$
11921	8385		7608			
11975	8348		7554			
12013	8321		7516			
12027	8311		7502			
12726	7855				368 only	
12735	7849					
12778	7823					
12813	7802					
12821	7797					
12859	7774					
13916	7183			7708	Same as 462	$^5D_2$-$^7F_3$
13997	7142			7627		
14050	7115			7573		
14087	7096			7537		
14125	7077		5404	Same as 510		$^5L_6$-$^7F_2$
14154	7062		5375			
14208	7035		5321			
14248	7016		5281			
14418	6933		5111			
14450	6918		5079			
14628	6834				368 only	
14715	6793					
14758	6773					
14781	6763					
14848	6732					
14884	6716					
14902	6708					
14956	6684					
14973	6676					
14987	6670					
15723	6358					
15787	6332					
15978	6256					
16010	6244					
16037	6233					
16071	6220					
16101	6208					
16235	6157			5389	Same as 462	$^5D_2$-$^7F_2$
16301	6132			5323		
16334	6120			5294		
16744	5970		2783	Same as 510		$^5L_6$-$^7F_1$
16792	5953		2736			
17406	5743				368 only	
18840	5306			2783	Same as 462	$^5D_2$-$^7F_1$
18924	5282			2700		
19529	5119	Absorption line				$^5L_6$-$^7F_0$
19822	5043				368 only	
19879	5028					
20008	4996					
20961	4769					
21041	4751					
21624	4623	Absorption line				$^5D_2$-$^7F_0$
23605	4235	uv-excited				
25097	3982	uv-excited				

[a] The numbers indicate the difference in cm^{-1} between the resonance level and the respective line.

[b] All the lines that appeared in 510 also are in 462, and all those that appeared in 510 and 462 appear in 368.

Table II. Wavelengths of the near-infrared lines from absorption data.

Wave Number (cm^{-1})	Wavelength[a] (Å)	Assignment
9282	10769	$^7F_4$-$^7F_0$
9535	10485	
9545	10474	
9867	10132	
10799	9258	$^7F_5$-$^7F_0$
10944	9135	
12123	8246	$^7F_6$-$^7F_0$
12253	8159	
12275	8144	
12307	8123	
12404	8060	
12411	8055	
12566	7956	
12575	7950	

[a] Data for the 10 000- and 8000-Å groups are from Gruber.[5]

Table III. Energy levels of AmIV and PuI.

	AmIV[a]			PuI[b]			
Term	Experimental (cm^{-1})	Calculated 5f hyd. (cm^{-1})	Calculation fitted (cm^{-1})	Expt. (cm^{-1})	Calc. (cm^{-1})	g exptl.	g calc.
$^7F_0$	0	47	40	0.00	0	0	0
$^7F_1$	2720	2667	2741	2203.55	2170	1.495	1.4976
$^7F_2$	5320	5288	5368	4299.55	4310	1.488	1.4855
$^7F_3$	7595	7561	7642	6144.34	6196	1.475	1.4764
$^7F_4$	9560	9523	9596	7774.45	7838	1.467	1.4687
$^7F_5$	10870	11148	11220	9179.05	9215	1.458	1.4588
$^7F_6$	12350	12206	12296	10238.24	10153	1.424	1.4329
$^5L_6$	19630	19048	19128				
$^5D_2$	21624	21831	21586				
$^5G_2$	21916	22360	22316				

[a] For AmIV the 5f hydrogenic values are $F_2 = 268.6$, $\zeta = 2605$ or $E_1 = 4031.5$, $E_2 = 20.5$, $E_3 = 392.8$. The fitted values are $E_1 = 4012.36$, $E_2 = 21.95$, $E_3 = 381.92$, $\zeta = 2614.17$ (all in units of cm^{-1}).

[b] The PuI calculations were for 5f wave functions and $F_2 = 230.6\ cm^{-1}$ and $\zeta = 2174.6\ cm^{-1}$, or a $\chi = \zeta/F_2$ of 9.43. The g values used in the LS limit had Schwinger corrections.

FIGURE CAPTION

Fig. 1. Plot of E/F_2 vs χ between $\chi = 9$ and 10.

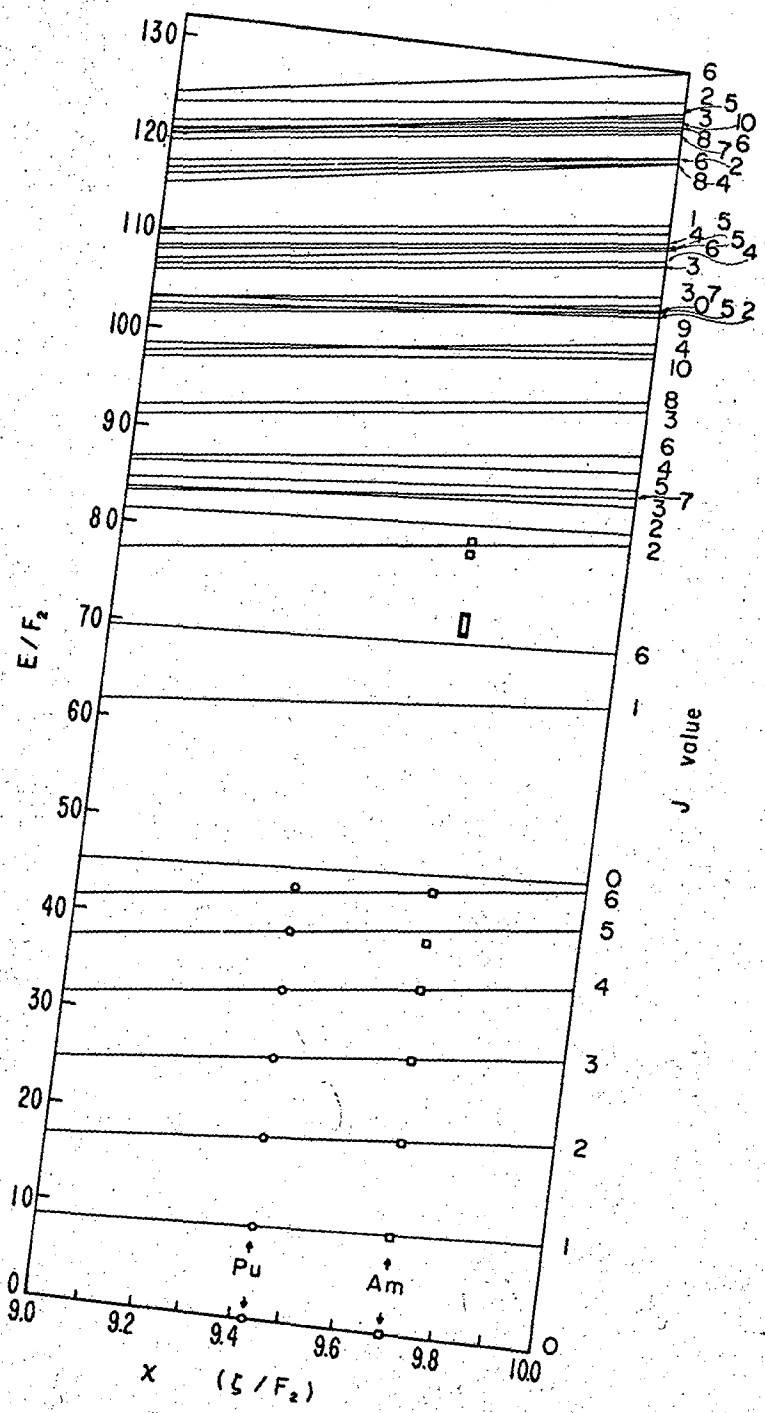
130
120
110
100
90
80
70
60
50
40
30
20
10
0
E/F₂
9.0
9.2
9.4
9.6
9.8
10.0
x (ζ/F₂)
Pu
Am
J value
MUB-2230

Fig. 1.