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ELECTRONIC STRUCTURE OF NEUTRAL AND SINGLY IONIZED CURIUM*

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ABSTRACT. Extensive observations and analyses of the emission spectra of neutral and singly ionized curium, Cm I and Cm II, have resulted in the determination of 785 Cm I and 598 Cm II energy levels. The levels found combine to classify 9145 of the more than 14,250 lines of ^{244}Cm observed between 240 and 2650 nm. Most of the levels have Lande g-values from Zeeman effect data and isotope shifts from measurements of spectra from sources with various enrichments of ^{244}Cm , ^{245}Cm , ^{246}Cm and ^{248}Cm . These data allowed us to assign many levels to specific electronic configurations. The ground configurations of Cm I and Cm II are $[\text{Rn}] 5f^6d7s^2$ and $[\text{Rn}] 5f^7s^2$, respectively. The relative energies of other electronic configurations of Cm are given and compared with analogous configurations in other actinides and in Gd its lanthanide analogue.

1. INTRODUCTION

There is now considerable knowledge of the electronic structure of neutral and singly ionized curium, Cm I and Cm II. This has resulted from our extensive observations and analyses of the curium emission spectrum. The analyses have yielded over 390 odd and 395 even levels of Cm I (most of these are published in Ref. 1) and over 434 odd and 164 even (nearly all unpublished) levels of Cm II. These odd and even levels of the two spectra combine to classify over 9145 or 64 percent of the more than 14,250 atomic emission spectrum lines of ^{244}Cm .

observed between 240 and 2650 nm. Most levels have Lande g-values from Zeeman effect data and almost all of the levels have known isotope shifts obtained from measurements of the spectra taken with sources enriched in various percentages of the isotopes ^{242}Cm , ^{244}Cm , ^{245}Cm , ^{246}Cm and ^{248}Cm (see Table I and Ref. 2). These data, especially the extensive isotope shift data, have permitted assigning a number of levels to specific electronic configurations and the g-values allow term assignments of the levels.

Table 1. Isotopic Composition of Curium Samples Used for Electrodeless Lamp Preparation.

Sample	Percent of Isotope (>1%)				Use
	244	245	246	248	
1	95	1.5	3		Wavelengths, Zeeman effect, spectrum assignment and reversal. Isotope shift on strong lines.
2	27		16	55	Isotope shift
3	55	23	21		Isotope shift

The analyses of these spectra has progressed to the point where all levels expected below $15,000\text{ cm}^{-1}$ have been identified in each spectrum. As is the case in all very complex spectra, many levels still remain to be found at high energies. However, the analyses are quite complete and give a very good description of the electronic structure of Cm I and Cm II.

2. RESULTS AND DISCUSSION

Levels belonging to the most important electronic configurations in the first, Cm I, and second, Cm II, spectra of curium have been determined. These configurations and the lowest identified level in each are given in Table II for Cm I and in Table III for Cm II. The configurations for each spectrum are grouped as odd or even according to spectroscopic rules. For the configurations considered here, a configuration is odd if the total number of f plus p electrons is odd and it is even if that total number is even. The energy of the lowest level for each configuration is given. In our discussion we will use the energy difference between the lowest levels as the energy difference between the electronic configurations. These differences will be representative of the promotion energy between configurations. Tables IV and V contain similar sets of data for Gd I and Gd II. In the tables the term designation, the Lande g-value and, in the case of Cm, the isotope shift $^{246}\text{Cm} - ^{244}\text{Cm}$ are given for each level.

Table II. Lowest levels of identified configurations in Cm I.

Configuration	Lowest Level (cm ⁻¹)	Desig.	Lande g-value	Isotope Shift (10 ⁻³ cm ⁻¹)
Odd				
5f ⁷ 6d 7s ²	0.00	⁹ D ₂	2.563	000
5f ⁷ 6d ² 7s	10144.93	11F ₂	2.873	-339
5f ⁸ 7s 7p	17656.63	⁹ D ₆	1.621	-463
5f ⁷ 6d ³	30443.92	11F ₂	2.53	-619
5f ⁷ 6d7s8s	34255.16	11D ₃	2.064	-220
Even				
5f ⁸ 7s ²	1214.18	⁷ F ₆	1.452	-279
5f ⁷ 7s ² 7p	9263.37	⁹ F ₃	2.112	+118
5f ⁷ 6d7s7p	15252.70	11F ₂	2.835	-269
5f ⁸ 6d7s	16932.72	⁹ G ₇	1.466	-586
5f ⁷ 6d ² 7p	32581.06 ^a	11G ₂	2.043	-527
5f ⁸ 7s8s	33013.09	⁹ F ₇	1.54	-460

^aLowest level of this configuration has not been found. It should be 11G₁ near 32000 cm⁻¹.

Table III. Lowest levels of identified configurations in Cm II.

Configuration	Lowest Level (cm ⁻¹)	Desig.	Lande g-value	Isotope Shift (10 ⁻³ cm ⁻¹)
Odd				
5f ⁷ 7s ²	0.00	⁸ S _{7/2}	1.935	000
5f ⁷ 6d7s	4010.66	10D _{5/2}	2.492	-496
5f ⁷ 6d ²	14830.15	10F _{3/2}	3.009	-962
5f ⁸ 7p	27065.11	⁸ F _{11/2}	1.51	-972
Even				
5f ⁸ 7s	2093.88	⁸ F _{13/2}	1.500	-738
5f ⁸ 6d	17150.79	⁸ G _{13/2}	1.415	-1177
5f ⁷ 7s7p	24046.39	10F _{7/2}	2.098	-403
5f ⁷ 6d7p	32034.44	10F _{3/2}	2.933	-923

Table IV. Lowest levels of identified configurations in Gd I. ^a

Configuration	Lowest Level (cm ⁻¹)	Desig.	Lande g-value
Odd			
4f75d 6s ²	0.00	9D ₂	2.651
4f75d26s	6378.15	11F ₂	2.980
4f75d ³	22429.16	11F ₂	
4f86s6p	25658.06	9D ₆	1.580
4f75d6s7s	31907.02	11D ₃	2.496
4f76s27s	34719.13	9S ₄	1.980
Even			
4f8 6s ²	10947.21	7F ₆	1.480
4f76s26p	13433.85	9P ₃	2.225
4f75d6s6p	14036.03	11F ₂	2.955
4f85d6s	24255.10	9G ₇	1.515
4f75d26p	25069.18	11G ₁	3.764
4f86s7s	40439.51	9F ₇	1.550

^aJ. Blaise, J.-F. Wyart and Th. A.M. Van Kleeef, C.R. Acad. Sc. Paris, 1970, 70, 261-263, and J. Blaise, J. Chevillard, J. Verges, J. F. Wyart and Th. A.M. Van Kleeef, Spectrochem. Acta, 1971, 268, 1-34.

Table V. Lowest level of identified configurations in Gd II. ^a

Configuration	Lowest Level (cm ⁻¹)	Desig.	Lande g-value
Odd			
4f75d 6s	0.00	10D _{5/2}	2.557
4f76s ²	3444.24	8S _{7/2}	1.920
4f75d ²	4027.16	10F _{3/2}	3.163
4f86p	32595.35	8D _{11/2}	1.565
Even			
4f86s	7992.27	8F _{13/2}	1.537
4f85d	18366.85	8G _{15/2}	1.465
4f76s6p	25668.69	10P _{7/2}	2.190
4f75d6p	25960.07	10F _{3/2}	3.095

^aJ. Blaise, J. F. Wyart and T. A.M. Van Kleeef, J. Phys. (Paris), 1971, 32, 617, and J. Blaise, J. Chevillard, J. Verges, J. F. Wyart and Th. A.M. Van Kleeef, Spectrochem. Acta, 1971, 268, 1-34.

Comparison of Tables II and IV and III and V show some similarities in the energies of like configurations for the two spectra of the elements but there are also some notable differences. The general ordering of the configurations considered here for the first spectra (Cm I and Gd I, Tables II and IV) is the same except for f^7d^3 . The 5d electrons are relatively more tightly bound in Gd than the 6d orbital electrons are in Cm. This is true in both the neutral and singly ionized configurations involving f^7 . More striking is the relative positions of configurations involving f^7 and f^8 . The even configuration $5f^87s^2$ in Cm I is only 1214 cm^{-1} above the $5f^76d7s^2$ ground configuration in Cm I while in Gd I $4f^86s^2$ is 10947 cm^{-1} above the equivalent ground configuration $4f^75d6s^2$. All equivalent f^8 configurations in Cm I are lower in energy by 7000 to 9000 cm^{-1} than the corresponding configurations in Gd.

Changes in the relative ordering of the electronic configurations because of differences in binding energies of orbital electrons in the two elements is more evident in the singly ionized or second spectra, Tables III and V. Here, the ground state of Cm II is $5f^77s^2$ some 4010 cm^{-1} below $5f^76d7s$ the configuration equivalent to the ground configuration in Gd II, $4f^75d6s$. The promotion energy f^7s^2 to f^8s is only 2094 cm^{-1} in Cm II while it is 4550 cm^{-1} in Gd II. As a result, the configuration ordering in Cm II is f^7s^2 , f^8s , f^7ds , f^7d^2 while in Gd II it is f^7ds , f^7s^2 , f^7d^2 , f^8s . The p orbital electrons do show some differences but not the marked differences exhibited by f and d orbital electrons.

Fig. 1 shows the relative positions of three electronic configurations each in neutral actinides and lanthanides. In the figure, the lowest level of the $f^{N-1}ds^2$ configuration is set at zero energy and the positions of the lowest levels of the f^Ns^2 and $f^{N-1}dsp$ configurations are shown. The promotion energy for s to p is about the same in the actinides as in the lanthanides and nearly constant across the series. This relationship and other trends in these and similar plots with more configurations are useful in the analyses of actinide and lanthanide spectra since estimates can be made of the position of unknown lowest levels of various configurations (dotted lines in the figure).

Fig. 1 shows that the f to d promotion energy changes considerably across the series. The general trend is for the f^Ns^2 configuration to become more stable as the series are ascended. The $5f^N7s^2$ configuration is less stable than $4f^N6s^2$ relative to $f^{N-1}ds^2$ for N less than or equal 7 but the opposite is true when N is equal to or greater than 8. Thus the two curves cross between N equal 7 and 8. The 5f orbital electron is more stable relative to the 6d orbital electron in the heavier actinides than is the 4f orbital electron relative to the 5d orbital electron in the heavier lanthanides.

The increased stability for the 5f orbital electron versus the 6d orbital electron is more clearly shown in Fig. 2 where the f^Ns^2 configuration is set at zero energy. This increased stability of the

5f orbital electron is related to the tendency toward divalent character for the higher members of the series found by nuclear chemists before the positions of the electronic configurations had been established by spectroscopists. Again, one can see that the promotion energy for 7s to 7p orbital electron is nearly constant while the 7s to 6d promotion energy increases across the series.

Fig. 1. Energy differences of the lowest levels of the $f^N s^2$ and $f^{N-1} dsp$ configurations relative to $f^{N-1} ds^2$ in the neutral or first spectra of some actinides (5f configurations--dark) and lanthanides (4f configurations--light).

Fig. 2. Energy of the lowest levels of several configurations relative to the lowest level of $f^N s^2$ in neutral actinides. In the configurations shown, the electrons are 5f, 6d, 7s and 7p. The increase in stability of the $f^N s^2$ configuration across the series is evident.

Only the lowest levels of various configurations have been shown thus far. A large number of complete terms have been found for many of the configurations of Cm I and Cm II. Table VI shows levels of the $5f^8 7s$ configuration of Cm II. This table clearly illustrates the value of isotope shift in making assignments of levels to configurations. The term assignments are made by use of the experimental Lande g-values. The constancy of isotope shift and the agreement of the observed g-values with values from theory or with the LS g-values substantiate the validity of the assignments.

Table VI. Low levels of the $5f^8 7s$ configuration of Cm II.

Level (cm^{-1})	J	g_{obs}	g_{LS}	a g_{calc}	ISO (mK)	Design.
2093.88	13/2	1.500	1.540	1.499	-738	8F
3941.46	11/2	1.424	1.455	1.432	-765	6F
5919.28	9/2	1.527	1.577	1.529	-736	8F
6347.92	11/2	1.500	1.554	1.495	-744	8F
7067.14	7/2	1.485	1.620	1.492	-748	8F
8144.32	9/2	1.400	1.435	1.404	-765	6F
8436.11	5/2	1.656	1.716	1.655	-733	8F
9073.60	7/2	1.444	1.398	1.439	-753	6F
9127.87	3/2	1.834	2.002	1.847	-733	8F
9801.32	1/2	3.740	4.007	3.739	-729	8F
10433.80	5/2	1.300	1.315	1.305	-763	6F
11250.911	3/2	1.167	1.067	1.155	-759	6F
11978.47	1/2	-0.420	-0.670	-0.425	-760	6F

^aJ. Blaise, J. F. Wyart, J. G. Conway and E. F. Worden, Phys. Scripta, 1980, 22, 224.

^bIsotope shifts are relative to the $5f^7 7s^2 \ 8s_{7/2}$ ground state. They are $^{246}\text{Cm}-^{244}\text{Cm}$ in mK ($1 \text{ mK} = 10^{-3} \text{ cm}^{-1}$).

The level structure of the lowest terms in Cm II are shown in Fig. 3. The electronic configurations and LS term designations are indicated. The structure of the levels of the $5f^8 7s$ configuration given in Table VI is more clearly illustrated in the figure. The closeness in binding energy of the 5f, 6d, and 7s orbital electrons is evident.

Fig. 4 shows the range of isotope shifts observed for assigned levels in the Cm I and Cm II spectra. It should be noted that there is overlap of observed shift for a number of configurations. In these cases, theory, Lande g-values, transition intensities and other factors are important for assigning the level to the appropriate configuration. As seen in the figure, we report the shifts relative to the ground state as x. For the shifts shown in Table II, III and VI, x is zero. The shifts are the frequency of ^{246}Cm minus the

frequency of ^{244}Cm . As is well known, the isotope shift is caused by interaction with the nucleus of the penetrating s orbital electrons and to a lesser extent by the $p_{1/2}$ electrons. Since f electrons act to shield or reduce the penetrations of the s and p electrons, the configurations with smallest isotope shift of those shown should be f^7d^3 and f^7d^2p in Cm I and f^7d^2 and f^8d in Cm II. Thus the value of α should be about $+0.7\text{ cm}^{-1}$ for Cm I and about $+1.2\text{ cm}^{-1}$ for Cm II.

Fig. 3. Low lying energy levels of singly ionized curium. The electronic configurations and LS term designations are given.

Fig. 4. Range of observed isotope shifts for several electronic configurations of curium I and II. The value of x is about $+0.7 \text{ cm}^{-1}$ for Cm I and about $+1.2 \text{ cm}^{-1}$ for Cm II.

Investigation of the isotope shifts with sources 2 and 3 listed in Table I were very important in obtaining reliable isotope shift values for the levels. The use of exposures from all three of these samples on the same plate made resolution of many confusing shifts on individual lines possible. By use of lines with large isotope shift and with negligible or no ^{245}Cm hyperfine structure, we were able to determine the relative isotope shift values shown in Fig. 5. The relative isotope shift for ^{242}Cm was obtained from data of Conway and McLaughlin.² For lines with small isotope shift more accurate $^{246}\text{Cm} - ^{244}\text{Cm}$ shifts could be calculated from the more accurately measured $^{248}\text{Cm} - ^{244}\text{Cm}$ shift and the relative isotope shift values. The odd-even staggering common in the actinides is shown by the position of ^{245}Cm in Fig. 5.

We show in Table VII a listing of papers dealing with observations of the atomic emission spectra and energy level analyses of Cm I and Cm II. The major contribution of each paper is noted in the Table. The early investigations 1 and 2 were limited by the small quantities of material, sources and spectrographs. The production of 2 mg of highly purified ^{244}Cm by E. K. Hulet, the use of electrodeless lamps as sources, the use of the 9.15 m grating spectrograph at Argonne National Laboratory with the associated high quality 2.4 T magnet, and finally the use of the Fourier Transform Spectrometer at Laboratory Aime Cotton all contributed to the successful acquisition of the very high quality data needed for the analyses of these complex spectra.

Table VII. Papers and reports on the atomic emission spectrum of curium, Cm I and Cm II.

Paper or Report	Major Contribution
1. J. G. Conway, M. F. Moore and W. W. T. Crane, <u>J. Am. Chem. Soc.</u> , 1951, <u>73</u> , 1308.	About 200 emission lines from a spark source 252 to 500 nm.
2. J. G. Conway and R. D. McLaughlin, <u>J. Opt. Soc. Am.</u> , 1956, <u>46</u> , 91.	Isotope shifts ^{244}Cm - ^{242}Cm of 183 lines on large spectrograph 305 to 525 nm. Energies of electronic configurations of neutral, singly, doubly and triply ionized actinides.
3. Leo Brewer, <u>J. Opt. Soc. Am.</u> , 1971, <u>61</u> , 1101 and <u>J. Opt. Soc. Am.</u> , 1971, <u>61</u> , 1666.	Analytical methods for impurities in Cm and Cm in Am.
4. R. H. Gaddy, <u>Applied Spectroscopy</u> , 1972, <u>26</u> , 49.	Energy levels of Cm I, 335 odd and 348 even levels, isotope shift, Zeeman effect, relative energies and isotopic shifts of configurations.
5. E. F. Worden and J. G. Conway, <u>J. Opt. Soc. Am.</u> , 1976, <u>66</u> , 109.	Atomic emission lines Cm I and II 850 to 2640 nm, energy levels, and energy level classification of lines. Wavelength, isotope shifts, g-value, intensities, spectrum assignment and energy level assignments for 2034 of the strongest ^{244}Cm lines of Cm I and II in the 240 - 1120 nm region.
6. J. G. Conway, J. Blaise and J. Verges, <u>Spectrochim. Acta</u> , 1976, <u>B31</u> , 31.	Emission spectrum of Cm I and II 242 to 701 nm. Wavelengths, intensities self-reversal. 6771 lines reported, no levels, some spectrum assignment. List contains over 800 impurity lines of Pu and lanthanides not found and eliminated by the authors of the paper.
7. E. F. Worden, E. K. Hulet, R. G. Gutmacher, and J. G. Conway, <u>Atom. Data and Nucl. Data Tables</u> , 1976, <u>18</u> , 459.	Curium isotope shifts ^{246}Cm - ^{244}Cm and ^{248}Cm - ^{246}Cm for 97 lines 404 to 693 nm. Wavelengths and intensities (Classifications taken from papers 5 and 7).
8. E. A. Lobikov, N. K. Odintsova and A. R. Striganov, "Emission Spectrum of Curium, Report IAE - 3210," I. V. Kruchatov Institute of Atomic Energy, Moscow, 1979.	
9. E. A. Lobikov, A. R. Striganov, V. P. Labozin, N. K. Odintsova and V. F. Pomytkin, <u>Opt. and Spectrosc.</u> , 1979, <u>46</u> , 596.

Fig. 5. Relative isotope shift for the atomic emission spectrum lines of five isotopes of curium.

III. ACKNOWLEDGEMENTS

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1. E. F. Worden and J. G. Conway, "Energy Levels of the First Spectrum of Curium, Cm I," J. Opt. Soc. Am., 1976, **66**, 109-121.
2. J. G. Conway and R. D. McLaughlin, J. Opt. Soc. Am., 1971, **46**, 91.