CRYSTAL AND SOLUTION SPECTROSCOPY OF EINSTEINIUM

MASTER

By

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HEAVY ELEMENTS RESEARCH GROUP

Chemistry Division

Argonne National Laboratory

CRYSTAL AND SOLUTION SPECTROSCOPY OF EINSTEINIUM

W. T. CARNALL

For presentation at the

SYMPOSIUM COMMEMORATING THE 25th ANNIVERSARY
OF THE DISCOVERY OF ELEMENTS 99 AND 100

at Lawrence Berkeley Laboratory
University of California
23 January 1978

Prof. G. T. Seaborg, Organizer and Chairman

A HERD OF SMALL WHITE DEER (A RARE MUTATION OF THE FALLOW DEER, DAMA DAMA) ROAM THE ARGONNE GROUNDS.
THE DRAWING ON THE COVER SHOWS THREE OF THESE UNUSUAL ANIMALS.

Crystal and Solution Spectroscopy of Einsteinium.*

W. T. Carnall, Heavy Elements Research Group, Chemistry Division,
Argonne National Laboratory

In a sense it is symbolic that papers on free-ion and condensed phase spectroscopy were chosen as the concluding work to be presented in this symposium. Einsteinium is probably the last element in the periodic table that will be available in sufficient quantity to permit the use of classical methods of spectroscopy to explore energy level structure⁽¹⁾. Indeed in both current and past attempts to observe absorption bands in solutions and crystals, the experimentalists have been pushing the use of classical methods and standard equipment to the limit in order to obtain interpretable results. This was certainly true of the first observation of the spectrum of Es^{3+} in solution⁽²⁾.

An innovative method of condensing the analyzing beam of a standard spectrophotometer on a microsphere of liquid made it possible for Cunningham and coworkers to obtain the first evidence of absorption bands characteristic of Es^{3+} , as shown in Fig. 1. The date was 24 January 1966, almost 12 years ago to the day. The date has additional significance to a number of us, because this was precisely the period during which investigators from

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spectra of Np^{3+} , Pu^{3+} , and Am^{3+} and extrapolating from there to Es^{3+} , and it is not too surprising that the estimates were wrong in important respects. As it turned out, the first $J = 5$ state is lower in energy than the first $J = 7$ state contrary to what we projected at the time.

Among the important experimental details required in just the first stage of improving the analysis was the relative energies of the first few excited states. Of particular interest was the energy of the first excited state. The group at ORNL addressed this problem in some very creative fluorescence experiments^(7,8). As described in a 1970 paper by Nugent, Baybarz, Werner, and Friedman⁽⁸⁾, Fig. 3, they excited fluorescence in an Es^{3+} -containing β -diketone chelate and detected emission near the limits of the spectral range they could investigate with their equipment. Correcting to aqueous solution, they assigned a $J = 7$ state at 9600 cm^{-1} . The assignment was based solely on our incorrect prediction. They would have been happy with $J = 5$.

The period 1969-1970 was also important for the report by Edelstein and coworkers⁽⁹⁾ at LBL of detecting Es^{2+} in CaF_2 by ESR methods. A self-luminescence spectrum of the sample was also published. In addition there was the deduction of II-III oxidation potentials for the actinides by Nugent and coworkers⁽¹⁰⁾. The intense charge transfer band observed in the spectrum of EsBr_3 provided an important benchmark in this work.

The next development in our understanding of electronic

structure in Es^{3+} took place at ANL. The group was finally successful in getting a sizeable sample of ^{253}Es away from the nuclear types long enough to make measurements of the solution absorption spectrum on a more macroscopic scale than had previously been attempted⁽¹¹⁾. Along with some increased intensity in the absorption bands compared to previous work, a new band was detected near 11000 cm^{-1} , Fig. 4. These data, along with those of Nugent and coworkers at ORNL, provided the basis for a significant improvement in the theoretical interpretation. It became possible at this point to introduce transition intensity as a guide to energy level assignment. Thus it was possible to avoid the semi-qualitative approach of matching calculated level energies with estimated band positions⁽¹²⁾. We measured the areas of the absorption band envelopes normalized to unit concentration and compared these intensities to those predicted by the Judd-Ofelt theory before making the energy level assignments. The pattern that emerged was consistent with all measurements made to date, and corresponded to the level structure yielded in Fig. 2 by constructing a vertical line at $F_2 = 288\text{ cm}^{-1}$.

In about 1974, the ORNL group began using a microscope-spectrophotometer system in conjunction with experiments in which compounds of Es were being synthesized and characterized. They succeeded in obtaining very clear absorption spectra of small samples such as that shown for EsBr_3 ⁽¹³⁾ in Fig. 5. These

spectra were the first taken in absorption in the solid phase, and the bands observed were consistent with those reported in solution. More recently, Fellows, Peterson, Young and Haire reported distinct changes in the spectrum of EsCl_3 reduced with H_2 at $\geq 575^\circ\text{C}$ ⁽¹⁴⁾. This, of course, is consistent with the formation of Es^{2+} .

In order to make further progress in the analysis of electronic structure in Es^{3+} , it was essential to be able to observe spectra recorded at low temperature, preferably at 4°K. Such measurements make possible a considerable simplification in the interpretation because all transitions arise from the lowest energy crystal field state. We could anticipate severe problems associated with the attempt to obtain such data from absorption measurements because of the radiation effects that tend to rapidly reduce transmission and the complexity due to the increasing presence of Bk^{3+} and Cf^{3+} over the time required for measurement.

At this point, Hessler, Caird and the group at ANL turned to laser excited fluorescence spectroscopy. We were beginning to develop a major facility with a variety of laser based capabilities in 1975, and many of the techniques that were being used proved to be well suited to the Es^{3+} problem. They provided the discrimination necessary to isolate Es^{3+} signals from those of its decay products. The predictions of the energy level structures of Bk^{3+} , Cf^{3+} , and Es^{3+} in LaCl_3 were also being

improved during this period based on a rapidly developing experimental base⁽¹⁵⁾.

We began by growing single crystals of LaCl_3 doped with Es^{3+} . This provides an environment of well established symmetry and minimizes interaction between Es^{3+} ions. The close proximity of Es^{3+} ions has the effect of broadening the observed spectral lines. The high resolution of a N_2 -pumped dye laser made it possible to scan the visible-near infrared region and selectively excite many of the Es^{3+} states even though Bk^{3+} and Cf^{3+} states were in close proximity as indicated in Fig. 6. The resulting fluorescence was monitored, and this can be done very sensitively. In this type of measurement most of the absorption and reemission occurs at the surface of the sample, so the fact that the sample may become opaque to transmission is not limiting. Further discrimination between levels characteristic of Es^{3+} and those of impurities became essential. It was provided by the measurement of fluorescence lifetimes coincidentally with monitoring the energies of the fluorescing states⁽¹⁶⁾.

The lifetimes of the observed fluorescence transitions are very characteristic, as indicated in Fig. 7. By appropriate electronic gating of the signals, one can detect the very weak fluorescence of Es^{3+} in the presence of very strong signals from Bk^{3+} and Cf^{3+} . Since there was independent evidence for the relative energies of lower-lying excited levels in Es^{3+} ,

Bk^{3+} , and Cf^{3+} (17), it was possible to obtain excitation spectra as well as fluorescence spectra.

In excitation spectra, the fluorescence of a well established state characteristic of Es^{3+} , for example the $J = 4$ state near 16500 cm^{-1} , is monitored, while scanning to a limited range of higher energies with the dye laser. In the absence of large ($>600\text{--}700 \text{ cm}^{-1}$) energy gaps, these states rapidly relax by non-radiative processes to the fluorescing $J = 4$ state following excitation. The signal is detected only when the pump energy is tuned to the energy of a higher-lying crystal field state of Es^{3+} . Excitation of Bk^{3+} or Cf^{3+} states will result in fluorescence at other energies⁽¹⁸⁾.

The block diagram in Fig. 8 shows the experimental arrangement. A 1-meter monochromator was used in the experiments to date, but the inherent resolution of the system exceeded by far the reproducibility of the wavelength drive. It was consequently necessary to introduce a diode trigger circuit so that the photomultiplier could be time-shared to record standard and sample spectra continuously⁽¹⁸⁾. The data from a typical recording is reproduced in Fig. 9. The only disadvantage to the method is that nature gives up her secrets very slowly.

The results given in Fig. 10 constitute a current status

report on the spectrum of $\text{Es}^{3+}:\text{LaCl}_3$. This represents the type of data desired for the whole spectral range. The confirmation that results when fluorescence from several different excited states decay to a single lower state is needed to accurately establish the details of the crystal-field splitting. In addition to the energies of levels, it is necessary to assign crystal field quantum numbers. These can be deduced if the polarization of the fluorescing transitions is known.

The selective excitation and fluorescence life-time monitoring techniques discriminated against impurities such as Bk^{3+} and Cf^{3+} . However traces of Pr^{3+} were also detected in every crystal even though the highest available purity La_2O_3 was used to produce the LaCl_3 . Not all impurities are unwelcome. The observed polarization of the Pr^{3+} lines revealed the orientation of the crystal host and thus provided the basis for assigning the polarization of the Es^{3+} lines.

Based on all of the experimental evidence obtained to date, it was possible to construct the complete ground state splitting diagram for $\text{Es}^{3+}:\text{LaCl}_3$ shown in Fig. 11. For comparison, the computed counterpart, which is still based on energy level parameters extrapolated from the analysis of lighter actinide energy level schemes is in quite good agreement. There is no question but that it will be possible to develop as complete an analysis of the energy level scheme for Es^{3+} as will be available for any of the lighter members of the series, but

the experiments are laborious and time consuming. Those primarily responsible for this work at ANL include J. P. Hessler, J. A. Caird, F. Wagner, Jr., R. K. Sjolom, and H. Crosswhite.

One of the advantages of the techniques we have been discussing is that they are well suited to very small samples. No attempt has been made to grow "mini"-crystals because to date it hasn't been necessary. We estimate that a few nanograms of Es^{3+} could be detected with relative ease, and this encourages at least the consideration of spectroscopic work with Fm^{3+} where the picogram scale is indicated⁽¹⁾.

In addition to a tentative energy level scheme for Fm^{3+} , as shown in Fig. 6, some guidance with respect to potentially prominent fluorescing lines is desirable. Actually we are able to make predictions of fluorescence branching ratios and radiative lifetimes since it has already been shown that several of the heavier actinides are amenable to an extensive intensity analysis. The theoretical model that provides the basis for computing intensities in good agreement with experiment can be used to predict the purely radiative relaxation characteristics of excited states. Typical results for Fm^{3+} are indicated in Fig. 12. For each excited state one can compute a total radiative lifetime and a branching ratio to each lower-energy state. Such a calculation maps the flow of energy in the system assuming that non-radiative processes are not rate controlling. A particularly interesting possibility

for monitoring characteristic fluorescence in Fm^{3+} is associated with the $^4\text{F}_{5/2}$ state predicted to lie near 18000 cm^{-1} . With a large energy gap to the next lower-lying state, the probability of rapid non-radiative decay is greatly diminished so the observed lifetime may be expected to approach the radiative limit. In addition, there is strong coupling to the ground state, so detectable fluorescence at $\sim 18000 \text{ cm}^{-1}$ would be predicted.

Experimentally, the problem would be to minimize the volume of the sample. It is probably not even necessary to separate from other actinide impurities; that can be accomplished by electronic discrimination. What is needed is to perform similar experiments with Es^{3+} to determine where the real problems lie and realistically appraise the chances of success in detecting Fm^{3+} .

I said at the beginning of this paper that the spectroscopy of Es required pushing the use of classical methods toward the limit. When you think about it, Burris Cunningham, Sherman Fried and all of their fellow micro chemists were faced with a similar type of problem as they began work on the Plutonium Project. They developed what to many were radical methods, and showed that they could productively work with the material available to them. In a sense, we have a similar challenge put to us today. Develop new, more sensitive methods of elec-

tronic structure analysis! Such methods will not only allow us to scale down from the microgram level, but will permit an increasingly detailed examination of the nature of the ionic environment which is fundamental to all chemical behavior.

The developments of the last 25 years in Es and Fm chemistry and spectroscopy are prologue. There are challenging new frontiers both today and for the future!

2/7/78 kek

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Figure Captions

- Fig. 1. The solution absorption spectrum of Es^{3+} . (Ref. 2,4)
- Fig. 2. Computed free-ion energy level scheme for Es^{3+} as a function of the electrostatic interaction parameter F_2 . (Ref. 11)
- Fig. 3. Schematic representation of the excitation of fluorescence in Es^{3+} - β -diketone chelate. (Ref. 7,8)
- Fig. 4. The solution absorption spectrum of Es^{3+} (Ref. 11)
- Fig. 5. Absorption spectrum of EsBr_3 (Ref. 13)
- Fig. 6. Computed free-ion states of Cm^{3+} , Bk^{3+} , Cf^{3+} , Es^{3+} , and Fm^{3+} (Ref. 15)
- Fig. 7. Relative life-times of some fluorescing states in $\text{Es}^{3+}:\text{LaCl}_3$ and $\text{Bk}^{3+}:\text{LaCl}_3$.
- Fig. 8. Block diagram of experimental equipment used in monitoring the excitation and fluorescence spectrum of Es^{3+} . (Ref. 18)
- Fig. 9. Absorption spectrum of $\text{Es}^{3+}:\text{LaCl}_3$ at 77°K with simultaneous recording of Fe-Ne wavelength standard spectrum.
- Fig. 10. Fluorescence transitions and life-times for $\text{Es}^{3+}:\text{LaCl}_3$.
- Fig. 11. Observed and computed ground state splitting in $\text{Es}^{3+}:\text{LaCl}_3$.
- Fig. 12. Fluorescence life-time and branching ratio calculation. for $\text{Fm}^{3+}:\text{LaCl}_3$.

FIRST OBSERVATION WITH $\sim 0.5 \mu\text{gm}$ ^{253}Es ON
24 JANUARY 1966 (CONFIRMED BY OBSERVATIONS WITH
 $\sim 2.8 \mu\text{gm}$) B.B. CUNNINGHAM, J.R. PETERSON, R.D. BAYBARZ,
T.C. PARSONS

ABSORBANCE

FIRST ABSORPTION SPECTRUM-MICROCELL WITH
 $\sim 3.5 \mu\text{gm}$ ^{253}Es D.K. FUJITA, B.B. CUNNINGHAM,
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THE SOLUTION ABSORPTION SPECTRUM OF Es^{3+}

FREE-ION ENERGY LEVELS OF Es^{3+}

L.J. NUGENT, R.D. BAYBARZ
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LUMINESCENCE OF Es^{3+} β -DIKETONE CHELATE
 $[\text{Es}^{3+}:\text{Cs Gd}(\text{HFA})_4 \leq 400 \text{ NANOGRAM } ^{253}\text{Es}]$

$9330 \text{ cm}^{-1} \xrightarrow{\hspace{1cm}} \sim 9600 \text{ cm}^{-1}$
 (CHELATE) CORRECTED (AQUEOUS SOLN)

J.P. YOUNG AND R.G. HAIRE ORNL

R.L. FELLOWS, M. NOE', J.R. PETERSON, UNIV. OF TENNESSEE

THE ABSORPTION SPECTRUM OF EsBr_3
AFTER ANNEALING AT 400°C

FREE-ION STATES OF THE HEAVY ACTINIDES

$\text{Es}^{3+} : \text{LaCl}_3$ Fluorescence Transitions and Lifetimes

FLUORESCENCE BRANCHING RATIO CALCULATIONS

FOR $\text{Fm}^{3+}:\text{LaCl}_3$

Initial State	Final State	Initial Energy (cm ⁻¹)	Final Energy (cm ⁻¹)	β_R	Excited State Lifetime msec
$^4\text{F}_{9/2}$	$\rightarrow$ $^4\text{I}_{15/2}$	8288	418	1.0	0.850
$^2\text{H}_{11/2}$	$\rightarrow$ $^4\text{I}_{9/2}$	9958	8288	.004	0.853
	$\rightarrow$ $^4\text{I}_{15/2}$		418	.996	
$^2\text{P}_{3/2}$	$\rightarrow$ $^2\text{H}_{11/2}$	12282	9958	.14	0.843
	$\rightarrow$ $^4\text{I}_{9/2}$		8288	.01	
	$\rightarrow$ $^4\text{I}_{15/2}$		418	.85	
$^4\text{I}_{13/2}$	$\rightarrow$ $^2\text{P}_{3/2}$	13382	12282	.0	0.143
	$\rightarrow$ $^2\text{H}_{11/2}$		9958	.02	
	$\rightarrow$ $^4\text{F}_{9/2}$		8288	.01	
	$\rightarrow$ $^4\text{I}_{15/2}$		418	.97	
$^4\text{F}_{5/2}$	$\rightarrow$ $^4\text{I}_{13/2}$	18776	13382	.05	0.190
	$\rightarrow$ $^2\text{P}_{3/2}$		12282	.02	
	$\rightarrow$ $^2\text{H}_{11/2}$		9958	.17	
	$\rightarrow$ $^4\text{F}_{9/2}$		8288	.05	
	$\rightarrow$ $^4\text{I}_{13/2}$		418	.71	