Lawrence Berkeley National Laboratory

Recent Work

Title

THE ABSORPTION SPECTRUM AND ZEEMAN EFFECT OF Am^{+3} IN LaCl_3

Permalink

<https://escholarship.org/uc/item/5w20f4z2>

Authors

Gruber, John B.
Conway, John G.

Publication Date

1961-06-01

UNIVERSITY OF
CALIFORNIA

Ernest O. Lawrence

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-9555
Revised

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

THE ABSORPTION SPECTRUM AND ZEEMAN EFFECT OF Am^{+3} IN LaCl_3
John B. Gruber and John G. Conway

June 1961

THE ABSORPTION SPECTRUM AND ZEEMAN EFFECT OF Am^{+3} IN LaCl_3

John B. Gruber and John G. Conway

Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

June 1961

ABSTRACT

The polarized absorption spectrum and Zeeman effect of Am^{+3} in LaCl_3 has been studied from 2000A to 8000A. In almost every instance the peaks or lines observed are sharp, completely polarized, and appear in definite groupings. For the particular point symmetry, C_{3h} forced electric-dipole-transitions are observed from 7F_0 to the excited crystal-field-split sublevels $\mu=\pm 2$ and 3 of J levels greater than one.

THE ABSORPTION SPECTRUM AND ZEEMAN EFFECT OF Am^{+3} IN LaCl_3 *

John B. Gruber and John G. Conway

Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

June 1961

INTRODUCTION

Although many investigators¹⁻³ have reported the solution spectra of Am^{+3} , relatively few papers have appeared in the literature on the solid state sharp line spectra of Am^{+3} . Stover and Conway in 1952 published part of the absorption spectrum of hydrated americium trichloride,⁴ and Iakovlev, Gorkenko--Germanov, Zenkova, Razbitnoi, and Kazanskii have reported a study of the absorption spectra of Am^{+3} in the double sulfates of potassium, thallium, rubidium, and cesium.⁵ In addition, Gruen, Conway, McLaughlin, and Cunningham have observed the fluorescence spectrum of Am^{+3} in LaCl_3 .⁶ Gruber has recently interpreted the infrared absorption spectrum from 0.79μ to 16μ as arising from transitions within the $7F$ multiplet.⁷

A detailed analysis of the energy spectrum is very much needed since it would reveal the multipolarity of the transitions observed and yield information on the quantum nature of the states of the free ion. In addition, a knowledge of the symmetry character, and the relative position of the crystal quantum sublevels of a crystal-field split J level, would give us some indication of the degree to which the field-free levels of Am^{+3} are split by the crystal field.

* This work was done under the auspices of the U. S. Atomic Energy Commission.

PREPARATION OF SINGLE CRYSTALS

Single crystals of $\text{AmCl}_3\text{-LaCl}_3$, containing Am^{+3} in amounts from 0.1 to 10% by weight, were prepared in the following manner. A known volume of Am^{+3} (americium-241; half life: 458 yr) in 2.0 M HCl was added to a quartz sublimation tube. The ion-exchange-purified Am^{+3} was found to be spectroscopically pure, and an α assay of the solution gave a reliable value for the concentration of americium. The solution was slowly evaporated on a vacuum line and anhydrous AmCl_3 formed by heating the hydrate slowly in the presence of dry HCl. After the tube was flushed repeatedly with dry argon, a known quantity of spectroscopically pure anhydrous LaCl_3 was added. The mixture was then thoroughly degassed and melted to form a solution. The sublimation and single-crystal growing techniques employed were quite similar to those reported by Sayre, Sancier, and Freed,⁸ and Gruen, Conway, and McLaughlin.⁹ The intense radioactivity of americium-241, as well as the hygroscopic nature of anhydrous LaCl_3 , requires that the crystal be mounted in a dry-nitrogen-atmosphere box suitably prepared for radioactive work.

In order to determine whether the $\text{AmCl}_3\text{-LaCl}_3$ mixed crystal system preserved C_{3h} symmetry about the cation sites, anhydrous PrCl_3 was added to the mixture before the single crystals were grown. When the absorption spectrum of the single crystal was taken, the Pr^{+3} lines were found to have the same polarization and energy positions as reported by Sayre, Sancier, and Freed.⁸ We conclude, therefore, that the symmetry about the Pr^{+3} ion is similar to that reported by Sayre, Sancier, and Freed, who had no Am^{+3} in their crystals, and that the symmetry about the americium ions very probably is C_{3h} . Also, the observed polarization spectrum of $\text{AmCl}_3\text{-LaCl}_3$ is consistent with the selection rules for C_{3h} .

SPECTROGRAPHIC EQUIPMENT

The absorption spectrum of the single crystals was taken with a Wadsworth-mount 3.4-m spectrograph. Two gratings were used in this instrument-- one with 7,500 lines per inch and another with 14,400 lines per inch. In the first order, the reciprocal linear dispersion was 10.1 Å/mm and 5.3 Å/mm, respectively. Crystals were maintained at selected temperatures of 77°K (liquid nitrogen) and 4°K (liquid helium) in quartz and pyrex dewars.

The Zeeman experiments were at fields of 28,750 and 37,000 gauss at temperatures of liquid nitrogen (77°K) and a dispersion of 5.3 Å/mm. A single experiment at 4°K and 28,750 gauss was performed but no sharpening of lines was observed.

THE POLARIZED ABSORPTION SPECTRUM

The polarized absorption spectrum of Am^{+3} in LaCl_3 was studied from 2000Å to 8000Å. In almost every instance, spectral lines observed are sharp and completely polarized. Definite groupings of lines appear in every portion of the spectrum.

For the particular point symmetry, C_{3h} , which is consistent with experiment, the polarized transverse and the axial spectra indicate forced electric-dipole transitions. Magnetic-dipole transitions are observed from 7F_0 (the ground level) to excited $J=1$ levels, and forced electric-dipole transitions are observed from 7F_0 to the excited crystal-field-split components $\mu=\pm 2$ and 3 of J levels greater than one. The quantum numbers, μ , have been defined by K. H. Hellwege,¹⁰ and the selection rules have been worked out by K. H. Hellwege,¹⁰ and Sayre, Sancier, and Freed.⁸

Many of the sharp lines in the visible and near-ultraviolet spectra split into two components in a Zeeman field. Thus, from the g values and the total number of allowed transitions to a given J manifold, we can establish a value for the field-free J level. The sublevels split in a magnetic field are indicated in Table I. Complications in the analysis of the Am^{+3} spectrum result from the intermediate coupling effects and the intermixing of crystal-field components of a given J level with those of J levels having nearly the same energy.

An additional handicap to interpretation, pointed out by Sayre and Freed is that of working with a crystal of C_{3h} symmetry and an ion of $J=0$ ground state.¹¹ All of these complications combine to make a positive assignment of L and S very difficult. The only sure assignments for Eu^{+3} , the rare earth antilog, are for the $^5D_{0,1,2}$. These levels are of very low intensity and in the case of Am^{+3} shifted to the infrared.¹² In the dilute crystals studied no levels were identified which could be assigned to the 5D multiplet. It would appear that pure crystals of Am salts would be needed to identify these levels.

The levels observed probably belong to the 5L , 5G , 5H , 5I , 5F multiplets but strong intermediate coupling prevents a simple direct correlation with the theoretical LSJ values.

Table I. Visible and ultraviolet absorption spectra, polarization, and intensities of Am^{+3} in Cl_3

Wave length (A) (in air) 77°K	Wave numbers (in vacuum) 77°K	$g = \frac{\Delta \nu}{2\beta H}$ $\Delta \nu$ = splitting between two Zeeman compo- nents	P Polarization	I Relative Intensity
5119.1	19,529	b	σ	7 ^a
5093.0	19,630	b	σ	10 ^c
5089.6	19,642	b	σ	4 ^d
5083.2	19,667		π	8 ^d
5075.0	19,699		π	10 ^c
4623.1	21,624	b	σ	5 ^e
4561.5	21,916	1.45	σ	8 ^{a,f}
4432.4	22,555		π	6 ^{a,g}
4305.0	23,222	b	σ	6 ^a
4298.7	23,256		π	4 ^{a,g}
4262.5	23,454		π	3 ^d
4260.0	23,468		π	3 ^h
4257.3	23,482		π	3 ^e
4245.2	23,549		π	7 ^h
4242.5	23,564		π	7 ^h
4239.9	23,579		π	7 ^h
4232.2	23,622	b	σ	7 ^d
4216.0	23,713	b	σ	6 ⁱ
4163.5	24,012	1.22	σ	4 ^{a,f}
4041.9	24,734		π	5 ^{g,j}
4041.1	24,739		π	2 ^{g,j}
4038.8	24,753	3.35	σ	6 ^{f,j}
3968.2	25,193	2.30	σ	4 ^{g,j}
3963.8	25,221		π	4 ^{f,j}

Table I. (continued)

Wave length (A) (in air) 77°K	Wave numbers (in vacuum) 77°K	$g = \frac{\Delta \nu}{2\beta H}$ $\Delta \nu =$ splitting between two Zeeman components	P Polarization	I Relative Intensity
3795.3	26,344	0.69	σ	9 ^d
3775.4	26,480		π	10 ⁱ
3773.0	26,497		π	4 ^d
3771.8	26,505		π	4 ^d
3765.0	26,553	2.58	σ	8 ^h
3759.5	26,592		σ	3 ^h
3754.3	26,629	5.07	σ	5 ^{a,f}
3745.7	26,690		π	3 ^d
3740.5	26,727		π	3 ^h
3732.6	26,783		σ	4 ^{b,i}
3658.2	27,328	2.68	σ	8 ^{a,f}
3632.7	27,520		σ	5 ^{a,f}
3629.8	27,542		π	7 ^a
3627.9	27,556	3.71	σ	6 ^{a,f}
3574.6	27,967		π	2 ⁱ
3418.5	29,244		π	4 ^e
3410.3	29,315		σ	4 ^e
3388.2	29,506		σ	4 ^e
3380.9	29,569		σ	4 ^e
3377.3	29,601		π	6 ^e
3155.0	31,687		σ	6 ^j
3153.2	31,705		π	6 ^j
3077.8	32,481		π	4 ^d
3067.7	32,588		σ	4 ^a
3060.1	32.669		π	4 ^d

Table I (Continued).

Wave length (A) (in air) 77°K	Wave Numbers (in vacuum) 77°K	$g_1 = \frac{\Delta \nu}{2\beta H}$ $\Delta \nu$ = splitting between two Zeeman compo- nents	P Polarization	I Relative Intensity
2994.4	33,386		π	3 ^j
2993.6	33,395		σ	3 ^a
2986.4	33,475		σ	3 ^j
2939.2	34,013		σ	6 ^a
2934.0	34,073		π	10 ^d
2916.4	34,279		σ	7 ^a
2914.0	34,307		π	7 ^a

^aLine width: 0.3 to 0.5A.

^bLine broadened in magnetic field.

^cUnresolved band structure.

^dLine width: 0.5 to 1.0A.

^eLine width: 2.0 to 5.0A: possible unresolved doublet.

^fAbsorption line split into two observable components in applied magnetic field.

^gLine not broadened in magnetic field.

^hLine width: 1.0 to 1.5A.

ⁱLine width: 1.5 to 2.0A.

^jLine width: 0.1 to 0.3A.

REFERENCES

1. D.C. Stewart, Absorption Spectra of Lanthanide and Actinide Rare Earths,
II. Transition Probabilities for +3 Ions in the Two Series,
Argonne National Laboratory Report ANL-4812, February 1952.
2. L.B. Asprey and T.K. Keenan, J. Inorg. Nucl. Chem. 7, 27 (1958).
3. J.J. Katz and G.T. Seaborg, The Chemistry of the Actinide Elements,
(Methuen and Company Ltd., New York, 1957).
4. B.J. Stover and J.G. Conway, J. Chem. Phys. 20, 1490 (1952).
5. G.N. Iakovlev, D.S. Gorkenko-Germanov, R.A. Zenkova, V.M. Razbitnoi, and
K.S. Kazanskii, J. Gen. Chem. USSR 28, 2653 (1958) (English translation).
6. D.M. Gruen, J.G. Conway, R.D. McLaughlin, and B.B. Cunningham, J. Chem. Phys.
24, 1115 (1956).
7. J.B. Gruber, submitted to J. Chem. Phys.
8. E. V. Sayre, K. M. Sancier, and S. Freed, J. Chem. Phys. 23, 2060 (1955).
9. D. M. Gruen, J. G. Conway, and R. D. McLaughlin, J. Chem. Phys. 25, 1102 (1956).
10. K. H. Hellwege, Nachr. Akad. Wiss. Gottingen, Math physik. KI. 37, 1947;
Ann. Physik (6), 4, 95 (1948); idem. (6) 4, 127 (1948); idem. (6) 4, 136 (1948);
idem. (6) 4, 143 (1948); idem. (6) 4, 357 (1949).
11. E. V. Sayre and S. Freed, J. Chem. Phys. 24 1211 (1956).
12. J. B. Gruber and J. G. Conway, J. Chem. Phys. 34 632 (1961).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.