



# LowTemperature Optical Absorption of Americium Halides

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## Low-Temperature Optical Absorption of Americium Halides\*

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Absorption spectra at low temperatures are reported for AmCl<sub>3</sub>, AmBr<sub>3</sub>, and AmI<sub>3</sub>. Bathochromic shifts have been generally observed in the series from the chloride to the iodide. These shifts are comparable to those observed in lanthanide halides. Hypersensitive transitions have been observed in AmI<sub>3</sub>. A number of new assignments of excited levels of Am(III) are proposed on the basis of intensity calculations. Electrostatic, spin-orbit, and configuration-interaction parameters were obtained by direct diagonalization and least-squares fitting to 29 observed levels for AmCl<sub>3</sub>. The parameter values in cm<sup>-1</sup> are:  $E^1=3582.8$ ,  $E^2=$ 17.276,  $E^3=334.30$ ,  $\zeta_{5f}=2593.3$ ,  $\alpha=21.634$ ,  $\beta=-158.48$ ,  $\gamma=1240.4$ .

#### INTRODUCTION

Most of the spectroscopic studies on actinide systems that have been reported to date have been carried out on solutions and single crystals.<sup>1</sup> It is also possible to gather significant information for  $f^N$  systems from diffuse-transmission studies of sublimed films. This has been shown in previous investigations on lanthanide cyclopentadienides.<sup>2</sup> In the present study the diffusetransmission technique has been used for a spectroscopic investigation of actinide halides at low temperatures.

Although the data obtained from sublimed films are not as precise or complete as those from single crystals, they are particularly useful in the case of systems for which single crystals are not easily available. They are also valuable for survey studies on a class of related compounds, such as the halides. In addition to reporting the experimental results for AmCl<sub>3</sub>, AmBr<sub>3</sub>, and AmI<sub>3</sub>, we present the results of a theoretical analysis of the free-ion energy levels of AmCl<sub>3</sub> which includes the effects of configuration interaction. The latter effects have been shown to be important in the interpretation of lanthanide spectra.<sup>3</sup>

#### **EXPERIMENTAL**

Anhydrous AmCl<sub>3</sub> was prepared by a modification of the original procedure due to Fried.<sup>4</sup> The preparation was carried out in a gloved box because of the radioactive hazard. Americium dioxide, obtained by heating <sup>243</sup>Am(OH)<sub>3</sub> at 700°C, was placed in a small reactor of rectangular Vitreosil tubing. The tubing had inner dimensions of 4 mm×8 mm and the outer walls were optically polished. The AmO<sub>2</sub> was mixed in the reactor with sublimed AlCl<sub>3</sub>. The system was exhausted and then filled with purified nitrogen. The reactants were

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slowly warmed until they melted to a brown liquid. After 90 min reaction at 220°C the liquid was cooled to room temperature. Unreacted AlCl<sub>3</sub> was removed from the system by sublimation under vacuum, as the temperature of the reactor was slowly raised. At 750°C AmCl<sub>3</sub> began to be transported. Sublimation was continued until a thin film of AmCl<sub>3</sub>, suitable for spectroscopic studies, coated the walls of the Vitreosil cell. The system was cooled to room temperature and the cell was sealed off under vacuum. AmBr<sub>3</sub> and AmI<sub>3</sub> were similarly prepared by reaction of AmO<sub>2</sub> in molten aluminum halides and sublimation at 700°

For low-temperature runs, the Vitreosil cell was indirectly cooled inside a double Dewar by thermal contact with a copper block which contained the refrigerant (liquid helium or liquid nitrogen) in its interior and by gas exchange with the refrigerant reservoir.

The double Dewar, provided with quartz optics, was fitted in the sample compartment of a Cary 14R spectrophotometer. A high-intensity quartz-iodine source was used both in the visible and in the near-infrared range of the instrument. In the near infrared, in spite of the high intensity of the source, the combination of amplification and noise level which was acceptable required slitwidths which were about an order of magnitude wider than the  $\sim$ 0.05 mm which was typical for the visible range.

Both in the visible and in the near ir to  $1.7 \mu$ , the light from the source was dispersed prior to incidence on to the sample. Hence, there were no objectionable heating effects of the sample in these ranges. This was especially important for the liquid-helium runs. In the remaining range investigated  $(1.7-2.6 \mu)$ , undispersed light from the standard Cary source fell onto the sample.

#### **RESULTS AND DISCUSSION**

A compilation of the observed band energies for the americium halides at liquid-helium temperature is given in Table I. The intensities of the various absorption peaks are also indicated. The data for each individual halide pertain to the same sample, run in a fixed con-

<sup>\*</sup> Based on work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup>W. T. Carnall and P. R. Fields, Advan. Chem. Ser. 71, 86 (1967). <sup>2</sup>R. Pappalardo and C. K. Jørgensen, J. Chem. Phys. 46, 632

<sup>(1967).</sup> <sup>8</sup> K. Rajnak, J. Chem. Phys. **43**, 847 (1965).

<sup>&</sup>lt;sup>4</sup> S. Fried, J. Am. Chem. Soc. **73**, 416 (1951).

		AmCl₂				AmBr <sub>3</sub>			AmI3	· · · · · · · · · · · · · · · · · · ·
Group	Level assignment <i>S'L'J'</i>	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )
·	7F <sub>0</sub> '	<u> </u>		0	·					
	7F1'			2 720ь						
Α	7F2'	5 308 5 375° 5 450°	85 5 6	5 308	5 238ª 5 308ª	2	5 270	$\begin{array}{c} 4 & 992 \\ 5 & 050 \\ 5 & 076 \\ 5 & 120 \\ 5 & 181 \\ 5 & 268 \\ 5 & 300 \\ 5 & 339 \\ 5 & 376 \\ 5 & 446 \end{array}$	8 29 100 20 18 5 6 11 8 5	5 100
В	7F3'	7 482 7 541	4 4	7 510	7 457ª 7 507ª	3 3	7 480	7 288 7 388 7 429 7 496	2 11 3 3	7 400
С	''F4'	9 305 9 374 9 457 9 533 9 598 9 774 9 870	$65 \\ 21 \\ 14 \\ \sim 100 \\ 15 \\ 3 \\ 6$	9 440	9 220d 9 256d 9 345d 9 385d 9 422d 9 470d.e 9 620d 9 691d 9 742 9 784	3 3 19 20 36 13 30 3 2 2	9 450	8 900 8 944 8 980 9 025 9 082 9 346 9 439 9 470° 9 503 9 586	3 7 35 8 3 2 58 16 13 9	9 210
D	7F5'	11 250 11 363	16 4	11 250	10 755ª 10 873ª 11 071ª 11 176ª 11 267ª	2 9 10 5	11 060	10 395 10 627 10 672 10 720 10 778	2 23 13 11 7	10 670
Е	7F <sub>6</sub> ,	12 307 12 500 <sup>d</sup> ,e	150 47	12 376	12 137 12 267 12 626 12 987	42 26 7 2	12 285	11 687 11 868 11 964° 12 500 12 680	4 95 11 5	11 930
F	<sup>5</sup> F <sub>0</sub>							15 180 15 220	2 2	
G	<sup>5</sup> D <sub>1</sub> ′							16 906 16 966	3 2	
н	5 <u>1</u> 6'	19 084 19 212 19 361 19 444 19 485' 19 646¤ 19 743° 19 810° 19 932	$     \begin{array}{r}       1 \\       2 \\       6 \\       15 \\       58 \\       \sim 250 \\       69 \\       19 \\       8     \end{array} $	19 627	19 256 <sup>t</sup> 19 297 <sup>t</sup> 19 323 <sup>t</sup> 19 353 19 413 <sup>t</sup> 19 450 19 485 19 523 <sup>s</sup> 19 558 19 576 19 588 19 635 19 693 19 720 19 755 19 810	12 21 27 14 45 21 23 64 64 27 20 12 2	19 500	19 022 19 102° 19 138h 19 153° 19 164° 19 205 19 230 19 249 19 271° 19 312 19 391 <sup>f</sup> 19 436 19 451 19 550 19 567° 19 627 19 735	$\begin{array}{c} 4\\ 92\\ 30\\ 22\\ 38\\ 44\\ 38\\ -130\\ 66\\ 90\\ 65\\ 10\\ 6\\ 3\\ 1\end{array}$	19 250

 
 TABLE I. Observed absorption peaks and centers of gravity of corresponding line groups in americium halides at liquid-helium temperature.

		AmCl <sub>3</sub>				AmBr <sub>3</sub>	······		AmI3	
Group	Level assignment S'L'J'	Peak energy (cm <sup>-1</sup> )	Absorb- anceª	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- anceª	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )
I	<sup>5</sup> D <sub>2</sub> ′	21 496 21 565° 21 593° 21 645 21 730	2 33 78 9 6	21 593	21 190 21 331 21 422 <sup>f</sup> 21 460 <sup>f</sup> 21 550	2 2 8 6 3	21 420	20 781 20 842 20 916 20 948' 21 000 21 070 21 120	2 2 8 23 8 6 3	<b>20 9</b> 50
I	⁵G₂′	21 853° 21 877' 21 934 22 016 22 133	62 5 5 4	21 877	21 640 21 668 <sup>4</sup> 21 786 21 882	4 7 2 2	21 670	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$28 \\ 14 \\ > 90 \\ 80 \\ 30 \\ \sim 90 \\ 42 \\ 50 \\ \sim 90 \\ \sim 100 \\ 82 \\ 20 \\ 90 \\ 18 \\ 7 \\ 18 \\ 7 \\ 18 \\ 7 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 $	21 500
J	5H3'	22 431 22 512 <sup>f</sup> 22 583 22 675 22 748	2 35 3 4 3	22 512	22 232° 22 245 22 371 22 426	5 9 8 3	22 300	22 002 22 065 22 116 22 222° 22 361 <sup>t</sup> 22 406 <sup>t</sup> 22 456 <sup>t</sup>	45 14 12 4 3 2 3	22 000
K	<sup>5</sup> H <sub>5</sub> '	23 176 <sup>f</sup> 23 211 <sup>f</sup> 23 291	34 14 20	(23 200)	22 967 23 009 <sup>f</sup> 23 094 23 130	4 34 22 23		22 727 22 826 <sup>t</sup> 22 873 22 935	5 55 25 15	
	5 <i>11</i> 4′	23 380 23 429 23 529 23 585 23 673 <sup>f</sup> 23 753 <sup>e</sup> 23 826 <sup>e</sup>	55 84 106 108 60 13 6	23 500	23 161 23 256 23 353 23 402° 23 430 23 526 23 574 23 710	24 32 18 25 34 18 11 3	23 250	23 068 23 105 23 164 23 207° 23 245t 23 300 23 364	16 14 14 16 59 17 10	23 050
K	<sup>5</sup> H <sub>7</sub> ′	23 975 24 024	14 4		23 787 23 838 <sup>4</sup> 23 992	4 6 2		23 524 23 635° 23 680 23 702 23 781	5 4 12 15 7	
L	<sup>5</sup> <i>L</i> 6′	24 722 24 777	26 2	24 722	24 480 <sup>f</sup> 24 570 24 636 <sup>f</sup> 24 783	5 5 16 2	24 550	24 096 24 200 24 248 24 300' 24 390 24 440 24 510	5 10 25 20 44 24 14	24 330
L	<sup>5</sup> D <sub>3</sub> ʻ	25 163 25 195 25 271 25 361	6 8 2 2	25 180	25 012 25 094 25 157 25 783	14 3 2	25 100	24 630 24 685 24 743 <sup>4</sup> 24 853 24 894 25 000	5 10 76 26 30 8	24 800
					25 940	2		20 000		

TABLE I (Continued)

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			AmCl₃			AmBr₃			AmI₃	
Group	Level assignment S'L'J'	Peak energy (cm <sup>-1</sup> )	Absorb- anceª	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )	Peak energy (cm <sup>-1</sup> )	Absorb- ance <sup>a</sup>	Center of gravity (cm <sup>-1</sup> )
M	5G4'	26 302 26 441 26 525 26 595 26 660 26 702	$\sim 80 \\ \sim 80 \\ \sim 80 \\ 44 \\ 24 \\ 28 \\ 40 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10$	26 540	26 082 26 274 26 434 26 455 26 581 <sup>4</sup> 26 620	42 43 17 23 20 17	26 250	25 458 <sup>i</sup> 25 550 <sup>i</sup> 25 641 <sup>i</sup> 25 743 <sup>i</sup> 26 021 <sup>i</sup>		
	•1.8	26 732 26 831 26 954°	40 19 6		26 639 26 690 26 752 26 795	23 17 13 7				
Ν	⁵G₂'	27 307	42	27 307	27 034 27 107	6 5	27 080			
0	<sup>5</sup> G <sub>5</sub> '	27 510 27 747	66 4	27 510	27 221 <sup>f</sup> 27 292	17 12	27 220			
	*D <sub>0</sub> ' *G*'	27 948	8	27 948	27 322 27 382	12				
Р	5L10'	28 264 28 352	3							
	<sup>5</sup> L <sub>9</sub> ' 5H7'	28 514 28 678 28 860	8 20 3		28 027 28 280	3 7				
Q	<sup>5</sup> H <sub>3</sub> ' <sup>5</sup> I <sub>4</sub> '	29 120 29 270	6 49	29 270	28 409 28 530 28 670	3 4 7				
	<sup>5</sup> <i>I</i> <sub>6</sub> ' <sup>5</sup> <i>F</i> <sub>1</sub> '	29 554	>75	29 554	28 802 28 968 29 070 29 163	10 14 22 22	29 250			
	<sup>5</sup> I5' <sup>8</sup> K5' <sup>5</sup> H4'	29 868 29 985	47 25	29 868 29 985	29 260 29 330 29 472 29 577 29 638 29 788 29 788 29 985 30 340	23 25 22 16 14 16 4 3				
	<sup>5</sup> G2' <sup>5</sup> D4' <sup>5</sup> He'	31 170 31 685 32 175	3 16 9	31 685	30 535 30 900 31 445	$\sim^{4}_{10}$				
	<sup>5</sup> G <sub>8</sub> ' <sup>5</sup> I <sub>8</sub> '	32 605	14		32 550 <sup>d</sup> ,i					
	<sup>5</sup> G₂') <sup>5</sup> K <sub>7</sub> '	21 072	1.0	32 605	34 250 <sup>d,i</sup> 36 230 <sup>d,i</sup>					
	<sup>5</sup> K <sub>6</sub> ' <sup>5</sup> K <sub>5</sub> ' <sup>5</sup> K <sub>8</sub> ' <sup>5</sup> F <sub>3</sub> '	32 873 33 422 34 036	14 14 50	32 873 33 422						
	<sup>5</sup> H <sub>4</sub> ' <sup>5</sup> G <sub>6</sub> ' 3 P. 1	34 270 34 566	31 25	34 150 34 674						
	$5F_{5}'$ $5H_{6}'$ $3O_{10}'$ $5P_{1}'$	34 770 35 088	23 40	35 088						
	<sup>•17'</sup> <sup>5</sup> D4'	36 700	~25							

TABLE I (Continued)

<sup>a</sup> In 10<sup>-2</sup> optical density units.
<sup>b</sup> Reference 13.
<sup>c</sup> Found only at low temperatures.
<sup>d</sup> At 78<sup>o</sup>K.
<sup>c</sup> Schoulder.

<sup>e</sup> Shoulder.

<sup>f</sup> Sharp absorption.

<sup>g</sup> Unresolved doublet. At 78°K, under better resolution, two peaks appear at 19 607 and 19 677 cm<sup>-1</sup>. <sup>h</sup> Very sharp.

<sup>i</sup> Broad band.

<sup>1</sup> Lines overlapping absorption edge.



FIG. 1. AmCl<sub>3</sub> at liquid helium. Line group A.

figuration first at room temperature, then at liquidnitrogen, and finally at liquid-helium temperature. For the purpose of the discussion to follow, the areas enclosed by the various line groups at liquid-helium temperature can be considered proportional to the corresponding intensities.

For all three americium halides studied, no significant changes in either the intensity or fine structure of the absorptions were noted in going from liquid-nitrogen to liquid-helium temperatures. On cooling the samples from room temperature, the peak heights usually increased. The room-temperature spectra were generally broader and their fine structure less clearly defined. Generally, the low-energy absorption tails were more extended at room temperature. Some room-temperature peaks were found to disappear or decrease in intensity on cooling.

Inspection of the general features of the spectra for the three halides shows that the  $\text{AmCl}_3$  spectra are simpler in appearance. The line groups of the remaining halides are much more complex and tend to have a larger energy spread (See Figs. 1–12). The intensities in the strong absorption groups tend to be concentrated in a few components in  $\text{AmCl}_3$ , while for the other two halides they are more evenly distributed amongst many components, especially in  $\text{AmBr}_3$ .

#### NEPHELAUXETIC SHIFTS

As expected on the basis of the nephelauxetic effect,<sup>5</sup> the individual line groups of the americium halides are generally shifted towards lower frequencies from the chloride to the bromide, and hence to the iodide. Evaluation of these shifts for Am(III) depends solely on locating the center of gravity of corresponding line

<sup>5</sup> C. K. Jørgensen, Orbitals in Atoms and Molecules (Academic Press Inc., London, 1962), p. 134.

groups since there is no crystal-field splitting of the ground level in this case. The centers of gravity can only be determined exactly when all of the individual Stark components of a group have been identified. Since this is not the case for the present data, the values of Table I must be taken as only indicative of the general trend. Richman and Wong<sup>6</sup> reported for Nd(III) in LaCl<sub>3</sub> and LaBr<sub>3</sub> nephelauxetic shifts ranging from  $\sim$ 10-150 cm<sup>-1</sup>, with an average shift of  $65 \text{ cm}^{-1}$ . The corresponding shifts in Am(III) are roughly twice as large. It should be noted, though, that in LaCl<sub>3</sub> and LaBr<sub>3</sub> both the symmetry and coordination number are unchanged, contrary to the case of AmCl<sub>3</sub> and AmBr<sub>3</sub>. The nephelauxetic shift for the group near 9000 cm<sup>-1</sup> from chloride to bromide seems exceptionally low. For this reason, we have explicitly indicated the appearance of this group in the three halides (Figs. 3) and 4). For the case of Pu(III), shifts of  $\sim 100 \text{ cm}^{-1}$ were observed<sup>7</sup> from La(C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O:Pu to LaCl<sub>3</sub>:Pu, although shifts of  $\sim 260 \text{ cm}^{-1}$  were also found.

The absorption edges in the three halides exhibited, as expected, analogous shifts. With the americium samples used, the region up to  $\sim 40\ 000\ \mathrm{cm}^{-1}$  was accessible for line detection in the chloride. This limit dropped to  $\sim 31\ 000\ \mathrm{cm}^{-1}$  for AmBr<sub>3</sub> and to  $\sim 25\ 500\ \mathrm{cm}^{-1}$  in AmI<sub>3</sub>. Some broad-band absorptions arising from a mechanism different from the  $5f \rightarrow 5f$  transitions are listed in Table I.

### VIBRONIC TRANSITIONS

The vibrational coupling of electronic levels has been investigated both in octahedrally coordinated U(IV)

<sup>&</sup>lt;sup>6</sup> I. Richman and E. Y. Wong, J. Chem. Phys. **37**, 2270 (1962). <sup>7</sup> H. Lämmermann and J. G. Conway, J. Chem. Phys. **38**, 259 (1963).





FIG. 4. Line group C: (a)  $AmBr_3$  at liquid nitrogen; (b)  $AmI_3$  at liquid helium.

complexes and in doped lanthanum chloride crystals.<sup>8-10</sup> The theory predicts that the intensity of vibronic bands in the absorption spectra of lanthanides (and actinides) will be proportional to the number of  $f^N$  ions coupled to the systems of lattice vibrations. Vibronic bands are then expected to be more important in undiluted lanthanide (or actinide) systems than in doped crystals.

Richman, Satten, and Wong<sup>9</sup> reported vibronic bands connected with some of the isolated electronic levels of Pr(III) (especially the  ${}^{3}P_{0}$  and  ${}^{3}P_{1}$  levels) in LaCl<sub>3</sub>: Pr,  $PrCl_{3}$ , LaBr<sub>3</sub>: Pr, and PrBr<sub>3</sub>. Since PrCl<sub>3</sub> and AmCl<sub>3</sub> both have the same UCl<sub>3</sub>-type structure, we can expect that the results for PrCl<sub>3</sub> will be applicable to AmCl<sub>3</sub>, with some contraction in the energy scale of the vibronic bands because of the larger mass of the Am ion.

In PrCl<sub>3</sub> Richman, Satten, and Wong<sup>9</sup> observed two vibronic bands ( $\sigma$  polarized) centered at ~80 and ~170 cm<sup>-1</sup> from the <sup>3</sup>P<sub>0</sub> electronic line and also a fairly narrow line at ~250 cm<sup>-1</sup>. A vibronic pattern comparable with the data on PrCl<sub>3</sub> is also observed for AmCl<sub>3</sub>. This pattern is characterized by isolated, fairly sharp peaks followed by broader bands. Typical vibronic patterns for AmCl<sub>3</sub> are shown in Figs. 1 and 7. Vibronic bands appear centered at  $\sim 65$ ,  $\sim 150$ , and possibly  $\sim 250$  cm<sup>-1</sup>. A similar vibronic pattern seems apparent in the absorption spectrum of AmI<sub>3</sub>. In the latter system most of the simpler line groups consist of a sharp intense absorption followed by weaker, broader peaks. In many cases, weak absorptions on the lowenergy side of the intense lines (which we assume to be the electronic transition) persist even at low temperatures. Three vibronic bands at  $\sim 45$ ,  $\sim 105$ , and  $\sim 185$ cm<sup>-1</sup> seem to be present in the AmI<sub>3</sub> line groups.

The appearance of the AmBr<sub>3</sub> spectrum does not



FIG. 5. Line group H for AmCl<sub>3</sub>: (a) at room temperature; (b) at 78°K.

<sup>&</sup>lt;sup>8</sup> S. A. Pollack and R. A. Satten, J. Chem. Phys. **36**, 804 (1962).

<sup>&</sup>lt;sup>9</sup> I. Richman, R. A. Satten, and E. Y. Wong, J. Chem. Phys. 39, 1833 (1963).

<sup>&</sup>lt;sup>10</sup> E. Cohen and H. W. Moos, Phys. Rev. 161, 258, 268 (1967).



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suggest a simple vibronic analysis. There are no easily identified vibronic patterns in the absorption of the kind found for AmCl<sub>3</sub> and AmI<sub>3</sub>. It is possible that in AmBr<sub>3</sub> the vibronic bands are more intense than the electronic transitions, but the evidence for this effect is limited. At least two line groups in AmBr<sub>3</sub> show roomtemperature satellites absent at low temperatures. The frequency shift of these "hot" vibronic bands was  $\sim 150 \text{ cm}^{-1}$  (Fig. 9).

#### **IDENTIFICATION OF THE LINE GROUPS**

In the following sections, we discuss the characteristics of the line groups in the three halides, with particular emphasis on the interpretation of results for AmCl<sub>3</sub>. Very detailed studies have been carried out on the lower-energy transitions observed in single crystals of Am(III) in LaCl<sub>3</sub> both in absorption (Refs. 11-13, henceforth referred to as I, II, and III, respectively) and fluorescence.13 Some assignments have also been made to the spectrum of Am(III) in aqueous and molten salt solutions.<sup>14</sup> The problem of level assignment is quite similar in its formulation to that encountered in the case of Eu(III), the lanthanide analog of Am(III).<sup>15</sup>

Usually the most precise and exhaustive information required for the identification of the J values for excited levels of  $f^N$  systems is supplied by the optical study of the relevant ion at a site of high point symmetry in a suitable host lattice. From Zeeman and polarization studies of single crystals, the J values of definite line groups can often be derived. A special situation obtains for the  $f^6$  configuration of Eu(III) and Am(III) in the LaCl<sub>3</sub> host lattice. As already pointed out by Sayre and Freed,<sup>16</sup> the selection rules for the  $f^6$  system in  $D_{3h}$  (and  $C_{3h}$ ) symmetry do not make it possible to discriminate between J=4, J=5, or J=6 values for the excited levels. Also, from the experimentally derived g values of the excited levels it is difficult to infer J values in a situation of intermediate coupling, as it occurs for Am(III). On the basis of studies on LaCl<sub>3</sub>: Am, Conway<sup>13</sup> identified the 10 lowest levels of Am(III) and obtained a two-parameter fit to the data with  $F_2 =$ 268.6 cm<sup>-1</sup> and  $\zeta_{5f} = 2605$  cm<sup>-1</sup>. Ratios pertinent to 5f-hydrogenic functions were used in order to estimate the  $F_4$  and  $F_6$  parameters. Under these conditions, the  ${}^{7}F_{1}$  group of Am(III) is located near 2700 cm<sup>-1</sup> above

<sup>&</sup>lt;sup>11</sup> J. B. Gruber, J. Chem. Phys. 35, 2186 (1961).

<sup>&</sup>lt;sup>12</sup> J. B. Gruber and J. G. Conway, J. Chem. Phys. 36, 191 (1962)

<sup>&</sup>lt;sup>13</sup> J. G. Conway, J. Chem. Phys. 40, 2504 (1964).

<sup>14</sup> W. T. Carnall and B. G. Wybourne, J. Chem. Phys. 40, 3428 (1964).

<sup>&</sup>lt;sup>15</sup> W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4450 (1968). <sup>16</sup> E. V. Sayre and S. Freed, J. Chem. Phys. **24**, 1211 (1956).

the ground level. This is in contrast with the known situation for Eu(III), where two J manifolds  ${}^{7}F_{1}$ and  ${}^{7}F_{2}$  are located approximately 200 and 1000 cm)<sup>-1</sup> above the ground level  ${}^7F_0'$  and so contribute to the optical absorption at room temperature.

The over-all splitting of the  ${}^{7}F$  term in Am(III) is in satisfactory agreement with the observed term splitting<sup>17</sup> in Pu(I)  $(5f^{6}7s^{2})$ , where the values of the relevant parameters are similar to those for Am(III).

Both AmCl<sub>3</sub> and LaCl<sub>3</sub> are UCl<sub>3</sub>-type structures.<sup>18</sup> Thus, one can tentatively assume that the model of an effective crystalline Hamiltonian possessing  $D_{3h}$  (or at least  $C_{3h}$  point symmetry, used in I in the discussion of Am(III) doped into LaCl<sub>3</sub>, can also be used for the case of AmCl<sub>3</sub>. This assumption is made in the following discussion to corroborate some of the level assignments and to correlate the spectra of AmCl<sub>3</sub> and LaCl<sub>3</sub>:Am.

In the analysis of the absorption spectra of the lanthanides in solution, we have found that intensity correlations provide a powerful tool in making J assignments.<sup>19,20</sup> Since relative intensities could be measured in the present investigation, a similar analysis was possible here. The basic calculations are closely related to those carried out for the Eu(III) aquo ion<sup>15</sup> and certain generalizations are possible. It can be shown<sup>21</sup> that since J=0 for the ground state of Am(III), induced electric-dipole transitions to excited levels where J' is zero or odd are forbidden. This selection rule exhibited a high degree of validity in Eu(III),<sup>15</sup> and thus one would predict that transitions to levels characterized by even values of J in Am(III) would at least tend to be more intense transitions. The expected variation in intensity in the transitions to the various J levels of the ground term has already been noted.<sup>22</sup>

Preliminary intensity calculations based upon approximate energy-level parameters14 made it possible to predict the relative intensities of the various allowed transitions. These predictions together with the assignments already established<sup>13</sup> provided a good starting point for the analysis of the spectrum of AmCl<sub>3</sub>. The more complex crystal-field effects in AmBr<sub>3</sub> and AmI<sub>3</sub> and the more limited region over which the spectra of these two compounds could be measured made the analysis of their spectra much more difficult. In the sections to follow, many of the band groups are tentatively identified in the three halides and spectral correlations discussed. The observed absorption peaks and the energies assigned to the various transitions are shown in Tables I and II. For convenience, we also list in Table II the reported absorptions of LaCl<sub>3</sub>: Am.

# GROUP A ( $\sim$ 5000 CM<sup>-1</sup>)

One intense line at 5307 cm<sup>-1</sup> ( $\sigma$  and axial) and two weaker  $\pi$ -polarized lines at 5208 and 5340 cm<sup>-1</sup> were reported in I. As shown in Fig. 1, the 5307-cm<sup>-1</sup> line agrees well with the band found in AmCl<sub>3</sub>, whereas the 5340-cm<sup>-1</sup> line occurs in the region in which we find weak bands, which we characterize as vibronic structure. We observe no absorption near 5208 cm<sup>-1</sup>. The group was assigned in III to the transition  ${}^7F_0' \rightarrow {}^7F_2'$ . (We adopt the convention of referring to the transitions in terms of the major component of the eigenvector of the levels. In many cases the level has <50% of the indicated character. Primed labels such as  ${}^{7}F_{4}$  are used as a reminder that the coupling is truly intermediate between the L-S and j-j coupling schemes and that little physical significance should be attached to the quantum numbers L and S. Only J remains as a good quantum number.<sup>14</sup> Other conventions are possible, but we wish to emphasize the foregoing.) The spectrum reported in I is not consistent with a transition to a J=2 level in either  $C_{3h}$  or  $D_{3h}$  symmetry.

In AmBr<sub>3</sub> only two bands could be detected over the noise level in this region of the spectrum (Fig. 2). In contrast, the absorption in AmI<sub>3</sub> is by far the most intense of the three halides and at least 10 individual components are present. Since this is a transition of a J=2 manifold, a maximum of five lines can be accounted for in terms of the splitting of the free-ion level. The intense absorption from 4990 to  $5180 \text{ cm}^{-1}$  contains five such components. The weaker system which follows could be a replica of the first group since five components are in evidence and their spacing is comparable with that of the first group. The band separation is estimated to be  $\sim 270 \text{ cm}^{-1}$ . The pattern of the absorption near 5070 cm<sup>-1</sup> appears to recur in many other absorption groups of AmI<sub>3</sub>.

#### GROUP B ( $\sim$ 7500 CM<sup>-1</sup>)

The weak absorption found for all three halides in this region is consistent with a forbidden transition. This group was not observed by Gruber in I but it has been reported in the absorption of nitrate melts<sup>14</sup> and in fluorescence in III. It was assigned in III to a  ${}^{7}F_{3}$  level. The two observed components (Table I) for AmCl<sub>3</sub> would be compatible with J=3 in  $D_{3h}$  symmetry, while three components would be expected for  $C_{3h}$ . The group in question is very weak and less-intense components might have been lost in the noise level. The general appearance of the AmI<sub>3</sub> band is guite reminiscent of the group at  $\sim$ 5070 cm<sup>-1</sup> in that medium.

# GROUP C (~9500 CM<sup>--1</sup>)

This group was studied in I by photographic techniques. It is interesting to compare the intensities

<sup>&</sup>lt;sup>17</sup> J. Blaise, M. Fred, S. Gerstenkorn, and B. R. Judd, Compt.

 <sup>&</sup>lt;sup>16</sup> J. Blanse, M. Fleu, S. Gersteinkolli, and D. R. Jude, Competender, Rend. 255, 2403 (1962).
 <sup>18</sup> R. W. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), Vol. 1.
 <sup>19</sup> W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. 40 (41069).

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<sup>49, 4424 (1968).</sup> <sup>21</sup> G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

<sup>&</sup>lt;sup>22</sup> W. T. Carnall and P. R. Fields, Develop. Appl. Spectry. 1, 233 (1962).

Tours	Center-	Am <sup>3+</sup> in LaCl <sub>3</sub> <sup>11-13</sup>		Calak	D. L.			Dand	Dand
assignment S'L'J' *	energy AmCl <sub>3</sub>	Obs Abs Am:LaCl <sub>3</sub>	Polariz	energy (cm <sup>-1</sup> )	for AmCl <sub>3</sub> (Abs×cm <sup>-1</sup> )	$U(\lambda)^{\mathfrak{c}}$	$\sigma U(\lambda)^{\mathfrak{s}} \ (\mathrm{cm}^{-1})$	for AmBr <sub>3</sub> (Abs×cm <sup>-1</sup> )	for $AmI_3$ (Abs $\times cm^{-1}$ )
7F0'	0			- 53					
7F1'		2720 5208ª		2727		0	0		
7F2'	5308	5307 5340	$\sigma \ \pi$	5338	25.5	0.0963	511	1.5	75
7F3'	7510			7584	2.0	0	0	1.1	6.9
7F4'	9440	9 282 9 535 9 545 9 867	σ π σ	9531	146.	0.1282	1210	59.	58.5
${}^{\eta}F_{5}{}^{\prime}$	11 250	10 799ª 10 944ª		11 159	17.2	0	0	34.	31.5
${}^{7}F_{6}'$	12 376	$\begin{cases} 12 & 253^{\circ} \\ 12 & 307^{\rm f} \\ 12 & 404^{\rm f} \end{cases}$	π σ σ	12 273	321.	0.2238	2770	134.2	185.
<sup>5</sup> <i>F</i> <sub>0</sub> ′				12 508			0		1.4
<sup>5</sup> <i>D</i> <sub>1</sub> ′				17 278			0		1.44
<sup>5</sup> L <sub>6</sub> ′	19 627	19 529 19 630 <sup>¢</sup> 19 642 19 667 19 699 <sup>¢</sup>	σ σ π π	19 605	508.	0.1920	3768.	141.6	246.
${}^{5}D_{2}'$	21 593	21 624	σ	21 586)	<b></b> .	0.0093)	}		
<sup>5</sup> G <sub>2</sub> ′	21 877	21 916	σ	21 883	70.4	0.0089	395.}	14.4	270.
<sup>5</sup> H <sub>3</sub> ′	22 512	22 555	$\pi$	22 487	20.6	0	0	7.8	47.8
<sup>5</sup> <i>H</i> <sub>5</sub> ′		23 222		23 279	~15.	0	0		
<sup>5</sup> //4′	23 500	$\mathbf{g}$		23 525	277.	0.0667	1567.	128.	104.
5H7'		24 012	σ	24 005	~12.	0	0		20.1
<sup>5</sup> <i>L</i> <sub>6</sub> ′	24 722	24 734 24 739 24 753	π π σ	24 680	14.2	0.0030	74.	9.6	69.
<sup>6</sup> D <sub>3</sub> ′	25 180	$\begin{array}{cccc} 25 & 193 \\ 25 & 221 \end{array}$	$\sigma \pi$	25 132	8.1	0	0	8.65	75.
<sup>6</sup> G4'	26 540	26 344 <b>b</b>		26 560	280	0.0458	1211.	121.8	200.
<sup>5</sup> L <sub>8</sub> ′		26 783	σ	26 768∫	200.	o∫	1211.	45.2	100.
<sup>5</sup> G <sub>2</sub> ′	27 307	27 328	σ	27 148	<b>Q4</b>	0.0054	147	31	280.
<sup>5</sup> G5'	27 510	27 520 27 542 27 556	$\sigma \ \pi \ \sigma$	27 608∫	71.	0.0004	11/1	51.	
<sup>5</sup> D <sub>9</sub> ′				27 826					
<sup>5</sup> G <sub>3</sub> ′	27 948	27 967	π	28 070	4.7	0	0		
<sup>5</sup> L <sub>10</sub> ′				28 392		0			
<sup>5</sup> L <sub>9</sub> ′				28 445		0			
5H7'				28 651	38.	0	0	13.6	
<sup>5</sup> H <sub>3</sub> '				29 054		0			

TABLE II. Energy assignments and calculated matrix eleme	nt of $U(\lambda)$ for AmCl <sub>3</sub> (anhyd) compared to data for Am(III) in Lal <sub>3</sub> ,C
Am	$Br_3$ , and $AmI_3$ .

Loval	Center-	Am <sup>3+</sup> in L	aCl <sub>3</sub> 11–13	Calab	Dand area			Rand area	Pand area
assignment S'L'J' *	energy AmCl <sub>3</sub>	Obs Abs Am:LaCl₃	Polariz	energy (cm <sup>-1</sup> )	for AmCl <sub>3</sub> (Abs×cm <sup>-1</sup> )	$U(\lambda)^{\mathfrak{v}}$	$\sigma U(\lambda) \circ (\mathrm{cm}^{-1})$	for AmBr <sub>3</sub> (Abs×cm <sup>-1</sup> )	for AmI <sub>3</sub> (Abs×cm <sup>-1</sup> )
<sup>5</sup> / <sub>4</sub> ′	29 270	29 244		29 320)		0.0019)			·····
<sup>5</sup> / <sub>6</sub> ′	29 554	29 315 29 506	σ σ	29 551		0.0094			
		29 569 29 601	σ π	ł	361.	ļ	276.	180.2	
<sup>5</sup> F <sub>1</sub> ' <sup>5</sup> I <sub>5</sub> '				29 676 29 769	-	0			
<sup>5</sup> Κ <sub>5</sub> ' 5 <i>Η</i> ,	29 868 29 985			29 847		0 0001			
5G2'	27 700			31 349)		0.0007)			
۰ ۵ <i>۵</i> ٫٬	31 685	31 687	σ	31 759	26.	0.0002	28.		
24	01 000	31 705	π	or 100)		0.0002)			
<sup>5</sup> H <sub>6</sub> '	32 175			32 234	21.	0			
<sup>5</sup> G <sub>3</sub> ′		32 481	π	32 349		0			
<sup>5</sup> <i>I</i> <sup>8</sup> ′		32 588	σ	32 425		0			
<sup>5</sup> G <sub>2</sub> ′	32 605	32 669	π	32 540	45	0.0020	44		
<sup>5</sup> K <sub>6</sub> ′	32 873			32 822∫	43.	0.0001	00.		
<sup>5</sup> K <sub>7</sub> ′				32 894		0			
<sup>5</sup> K <sub>5</sub> ′	33 422	33 386 33 395 33 475	π σ σ	33 333	21.	0	0		
<sup>5</sup> K <sub>8</sub> ′			-	33 542		0			
<sup>5</sup> H <sub>3</sub> ′				33 920		0			
<sup>5</sup> H <sub>4</sub> ′	34 150	34 013 34 073 34 279 34 307	σ π σ π	34 197	170.	0.0084	287.		
<sup>5</sup> G <sub>6</sub> ′	34 674			34 720		0.0016	55.		
<sup>5</sup> F <sub>5</sub> ′				34 815					
<sup>5</sup> D <sub>1</sub> '				34 816					
°H <sub>6</sub> ′	35 088			35 021		0.0008	28.		
°U <sub>10</sub> ′				35 428					
°F1' 67_1				35 490					
5D4'				36 419		0.0048			
5G5'				36 866		0.0040			
<sup>5</sup> K <sub>9</sub> ′				37 233		õ			
<sup>5</sup> H3'				37 293		0			
${}^{8}M_{8}'$				37 478		0			
<sup>5</sup> <i>H</i> 7′				38 139		0			
<sup>5</sup> G4'				38 185		0.0006			
<sup>5</sup> D <sub>2</sub> '				38 513		0			
°/V9′ ≸⊅D •				38 598		0			
۳.00° ۲.10				38 726		0			
-114'				39 301		$\sim 0$			

TABLE II (Continued)

<sup>a</sup> Major component of the eigenvector. No assignment is implied unless a center-of-band energy in AmCl<sub>3</sub> is given. <sup>b</sup> Based upon experimental results for AmCl<sub>3</sub>, the parameters used to

 ${}^{7}F_{2}', U(2) = 0.0963, U(4) = 0, U(6) = 0, \text{ etc.}$ d Not observed in AmCl<sub>2</sub>.

Based upon experimental results for thirds, the parameters used to generate this set were  $E^1 = 3582.8$ ,  $E^2 = 17.276$ ,  $E^3 = 334.3$ ,  $\zeta = 2593.3$ ,  $\alpha = 21.634$ ,  $\beta = -158.48$ ,  $\gamma = 1240.4$ .  $^{\circ}U(\lambda) = (\psi J || U^{(\lambda)} || \psi' J')^2$ , where  $\lambda = 2, 4, 6$ . For 5f<sup>6</sup>,  $U(\lambda) = 0$  except

<sup>e</sup> Fight lines observed 12 123-12 575 cm<sup>-111</sup>; only the three most prominent are recorded here.

<sup>f</sup> Unresolved band structure.

where  $\lambda = J'$ , the J value of the excited state, i.e., for the transition  $F_0' \rightarrow$ 

<sup>g</sup> Eleven lines reported in Ref. 11 in this range. <sup>h</sup> Nine lines observed 26 344-26 727 cm<sup>-1</sup>.<sup>12</sup>

derived by that technique with those observed for AmCl<sub>3</sub> (Table I). By the former method the ratio of the intensity for the line at 9533 cm<sup>-1</sup> to that at 9870 cm<sup>-1</sup> is two, while from Table I the ratio of the corresponding band intensities is > 15. In both LaCl<sub>3</sub>: Am and AmCl<sub>3</sub>, if the absorption near 9870 cm<sup>-1</sup> (Tables I and II) is included in the group, the crystal splitting would be quite large,  $\sim 600$  cm<sup>-1</sup>. This seems rather unlikely. If the absorption near 9870 cm<sup>-1</sup> does not belong to the group, then the polarized absorption in LaCl<sub>3</sub>: Am would be consistent with a J=4 level in  $D_{3h}$  symmetry (Table II). Inclusion of this line would lead instead to a  $C_{3h}$  symmetry.

The complex appearance of the AmCl<sub>3</sub> spectrum shown in Fig. 3 can be explained by assuming that each intense line is accompanied on the high-energy side by two weaker components, separated by  $\sim$ 70 and  $\sim$ 150 cm<sup>-1</sup>. This would agree with the pattern of Fig. 1. The sharpening of the bands in this group, due to cooling of the sample from 298 to 78°K, is also shown in Fig. 3.

Some pecularities in the positions of this group were already mentioned in connection with the nephelauxetic shift. The group appears to consist of two bands in all three halides. The separation of the two component bands is  $\sim 200 \text{ cm}^{-1}$  in chloride and bromide, but more than twice that in the iodide as shown in Fig. 4. The AmBr<sub>3</sub> shows a vanishing or negative shift from AmCl<sub>3</sub>. One of the component bands in AmI<sub>3</sub> is shifted to lower energy from the corresponding band in AmBr<sub>3</sub> by  $\sim 500 \text{ cm}^{-1}$  and shows a "group-A" pattern.

#### GROUP D (~11 300 CM<sup>-1</sup>)

This group was not reported in I. Very weak lines at 10 800 and 10 947 cm<sup>-1</sup> were found in III and assigned to the  ${}^{7}F_{0}' \rightarrow {}^{7}F_{5}'$  transition. Carnall and Fields found very weak peaks in this region, in the case of Am(III) in molten nitrate melts.<sup>22</sup> In AmCl<sub>3</sub>, the absorption bands in this region were found at higher energies than those reported in III (Table I). The AmCl<sub>3</sub> absorption group has less spread than that of the corresponding groups in the other two halides. The shift in energy from the chloride to the iodide (~600 cm<sup>-1</sup>) is particularly large in this case.

### GROUP E (~12 000 CM<sup>-1</sup>)

Eight lines were recorded in I for this group, which was ascribed to an overlap of transitions to a J=5 and a J=6 level. The group was simply identified as a J=6 level in III. Only two peaks were resolved in the AmCl<sub>3</sub> spectrum in this region.

The absorption pattern is similar in the three halides (Table) I but both the bromide and iodide have weaker absorption bands toward higher energy beyond the spread of the AmCl<sub>3</sub> band. In the case of the iodide, the weaker band near 12 600 cm<sup>-1</sup> looks like a replica of the

more intense absorption centered near 11 900 cm<sup>-1</sup>. The bands at  $\sim 12000$  cm<sup>-1</sup> could be due to the  ${}^{7}F_{0}' \rightarrow {}^{5}F_{0}'$  transition.

#### GROUPS F AND G

Preliminary calculations predicted a J=0 level near 12 500 cm<sup>-1</sup> and a J=1 level near 17 100 cm<sup>-1</sup>.<sup>13,14</sup> We assume that the J=0 level occurs within the band due to the transition from  ${}^7F_0'$  to  ${}^7F_6'$  for AmCl<sub>3</sub> or in the proximity of this band in the bromide and iodide. No bands were found in the region  $\sim 13 000-19 000$  cm<sup>-1</sup> in either AmCl<sub>3</sub> or AmBr<sub>3</sub>. In the iodide, two weak absorptions appear at 15 200 and 16 900 cm<sup>-1</sup> (Table I). It is possible that these do correspond, respectively, to the transitions to the predicted J=0 and J=1 levels, although as was indicted above the transition to J=0 is predicted at a much lower energy. Comparison with the spectra of NpI<sub>3</sub> and PuI<sub>3</sub> indicates that neither Pu nor Np impurities in the AmI<sub>3</sub> could account for the absorptions in question.

#### **GROUP H** ( $\sim$ 19 600 CM<sup>-1</sup>)

The general appearance of this group in AmCl<sub>3</sub> is similar to that of group E. Five main absorption lines were reported for this group in II, where two of the lines showed unresolved band structure (Table II). The four most intense lines have a polarization compatible with electric-dipole transitions to a J=6 level in  $C_{3h}$  symmetry. The group has been identified by Conway<sup>13</sup> as  ${}^{5}L_{6}'$ .

The transition has a very high molar absorptivity<sup>22</sup> in aqueous solution ( $\epsilon \sim 400$ ), i.e., about an order of magnitude larger than the molar absorptivities of  $3d^N \rightarrow 3d^N$  transitions. The distinct lines reported in II correspond in energy to the region of maximum intensity as observed in AmCl<sub>3</sub>. Peaks not reported in II or III clearly appear on both sides of the band in AmCl<sub>3</sub>. The two peaks at 19 876 and 19 938 cm<sup>-1</sup> (Fig. 5) could be explained as  $\sim 250$ -cm<sup>-1</sup> overtones of the two peaks at  $\sim 19$  607 and 19 677 cm<sup>-1</sup>, respectively, as observed at 78°K. The weak absorptions appearing at the threshold of the band (Table I) cannot be explained in a simple model which neglects the effects of neighboring ions and vibronic interactions.

The intense transition to  ${}^{5}L_{6}'$  is similar in the bromide and the iodide (Fig. 6). Both groups are very complex and rich in lines. The bromide spectrum is very reminiscent of the Am double-sulfate spectra observed by Yakovlev and co-workers.<sup>23</sup>

<sup>1</sup> The over-all spread of the group is largest in the bromide, where it spans  $\sim 500 \text{ cm}^{-1}$ ; this is to be contrasted with the very intense but narrow absorption of AmCl<sub>3</sub> (full width at half-height:  $\sim 150 \text{ cm}^{-1}$ ).

<sup>&</sup>lt;sup>23</sup> G. N. Yakovlev, D. S. Gorbenko-Germanov, R. A. Zenkova, V. M. Razbitnoi, and K. S. Kazanskii, J. Gen. Chem. USSR **28**, 2653 (1958).

#### GROUP I (21 600 and 21 900 CM<sup>-1</sup>)

The group in question, as shown in detail in Fig. 7, consists in AmCl<sub>3</sub> of two strong, sharp absorptions followed by numerous weaker bands. Two lines were found in this region in II. Both were  $\sigma$  polarized and broadened or split in a magnetic field (Table II). Each observed line is consistent with an electric-dipole transition to an excited J=2 level, either in  $D_{3h}$  or  $C_{3h}$ symmetry. A very similar pattern is found in AmCl<sub>3</sub>. Each isolated strong line shows a possible doublet structure, with the indication of a shoulder on the lowenergy side (Fig. 7). Each sharp line is followed by a continuum with peaks separated from the main absorption by distances comparable with the  $\sim 70$  and  $\sim$ 170 cm<sup>-1</sup>, already noticed in the case of Figs. 1 and 3. The group at 21 600 cm<sup>-1</sup> was assigned in III to a  ${}^{7}F_{0}' \rightarrow {}^{5}D_{2}'$  transition and the group at 21 900 cm<sup>-1</sup> to the  ${}^{7}F_{0}' \rightarrow {}^{5}G_{2}'$  transition. Both groups, incidentally, satisfy the  $\Delta J = 2$  condition for hypersensitivity,<sup>20</sup> and a disproportionate increase in intensity in this region was observed experimentally in the spectrum of Am(III) in a molten nitrate salt solution.<sup>22</sup> This is discussed further in a later section on hypersensitivity. The intensity of the AmBr<sub>3</sub> bands in this group appears normal, but those of AmI<sub>3</sub> were found to be disproportionately intense, indicating a situation similar to that observed in the nitrate melt. The spectra are shown in Fig. 8.

Implicit in the assignment (Table I) of corresponding groups in the three halides in this region is the assumption of a large shift ( $\sim$ 700 cm<sup>-1</sup>) from chloride to iodide. Both iodide groups corresponding to J=2 levels (Table I) have a number of component lines in excess of the maximum permissible number, in the absence of vibronic interactions. The iodide group at  $\sim$ 20 950 cm<sup>-1</sup> shows a marked similarity with Group A at  $\sim$ 5070 cm<sup>-1</sup>.

# GROUP J (22 500 CM<sup>-1</sup>)

The next isolated single line in AmCl<sub>3</sub>, as shown in Fig. 7, strongly resembles the two previous ones but is characterized in LaCl<sub>3</sub>: Am by  $\pi$  polarization (Table II). In the  $D_{3h}$  or  $C_{3h}$  point groups, a single  $\pi$ -polarized line would indicate a magnetic dipole transition from the ground state to a J=1 level. If such were the case, the line should broaden or split in a magnetic field. This was not observed in II. Also, on the basis of preliminary calculations it is clear that no J=1 levels are predicted in this energy range. The alternative assignment, compatible with the energy-level calculations, would involve a J=3 level. In this case the selection rules give two lines in  $D_{3h}$  symmetry, one  $\sigma$  (an axial) and one  $\pi$ , while three lines, one  $\sigma$  (and axial) and two  $\pi$ , are predicted for  $C_{3h}$  symmetry.

In AmBr<sub>3</sub>, Fig. 8, two resolved bands are observed in

the range 22 200–22 500 cm<sup>-1</sup>. In the iodide a single more intense band is found at  $\sim$ 22 000 cm<sup>-1</sup>, suggesting a chloride-to-iodide shift of  $\sim$ 500 cm<sup>-1</sup> if the correspondence is correct.

# GROUP K ( $\sim 23500$ CM $^{-1}$ )

This absorption is very complex, both in AmCl<sub>3</sub> and in LaCl<sub>3</sub>: Am. No assignments have been suggested, and very little can be inferred from polarization or Zeeman splitting of the lines in II (Table II). Preliminary calculations indicated transitions to J=5, J=4, and J=7 levels in this energy range. The transition to J=4may be expected to be the most intense of the three, as mentioned earlier. Characteristically, most of the lines reported in LaCl<sub>3</sub>: Am are  $\pi$  polarized.<sup>12</sup> Six of these  $\pi$ -polarized lines are followed by two  $\sigma$ -polarized lines.

As shown in Fig. 9 the satellite line at 22 836 cm<sup>-1</sup> in AmBr<sub>3</sub> disappears on cooling. The weak group at  $\sim 22 400 \text{ cm}^{-1}$  in AmI<sub>3</sub> (Fig. 8) does not fit well in the general group assignment. The rest of the group shows normal nephelauxetic behavior in the three halides. In AmI<sub>3</sub> the two composite groups with maxima at  $\sim 22 830$  and  $\sim 23 245 \text{ cm}^{-1}$  (Table I) show a very similar structure. Each intense peak is followed by weaker components at  $\sim 50$  and  $\sim 110 \text{ cm}^{-1}$ . Again, the iodide group at  $\sim 22 830 \text{ cm}^{-1}$ .

# GROUP L ( $\sim 24700$ CM<sup>-1</sup>)

Three polarized lines were reported in II near 24 700 cm<sup>-1</sup> (Table II). Preliminary calculations indicate that the group should be identified with a transition to a J=6 level. The indicated polarizations would not be consistent with this assignment in either  $C_{3h}$  or  $D_{3h}$  point symmetry. A single, isolated band is found in AmCl<sub>3</sub>.

A more widely split group centered near 24 560 cm<sup>-1</sup> is found in AmBr<sub>3</sub> (Fig. 10), and this group appears to have shifted to  $\sim$ 24 350 cm<sup>-1</sup> in AmI<sub>3</sub>.

A very weak band with two resolved components at  $\sim 25\ 163$  and  $\sim 25\ 195\ {\rm cm}^{-1}$  is found in AmCl<sub>3</sub> corresponding to two lines reported in II at 25 193 and 25 221 cm<sup>-1</sup> (Table II). The  $\pi$ -polarized line was found to split in a magnetic field. This suggests a magnetic-dipole transition to a J=3 level, which would be consistent with the observed polarization of the lines and with approximate energy-level calculations but would conflict with the  $\Delta J$  selection rules for magnetic-dipole transitions.

In both AmBr<sub>3</sub> and AmI<sub>3</sub>, corresponding groups may be identified near 25 100 and 24 800 cm<sup>-1</sup>, respectively (Fig. 10).

#### GROUP M (~26 500 CM<sup>-1</sup>)

The next group in AmCl<sub>3</sub> extends from  $\sim 26\,300-26\,800\,\mathrm{cm}^{-1}$  (Fig. 11) and shows considerable intensity

at the energy where we expect to find transitions to a J=4 level and a J=8 level (Table I). Most of the intensity should arise from the former transition. A number of lines were reported in II to occur in this region (Table II). The splitting in AmBr<sub>3</sub> is larger, and the leading edge of the absorption appears to be shifted  $\sim$  300 cm<sup>-1</sup> lower than that of the chloride (Fig. 11). In this region we began to observe an intense absorption edge in the AmI<sub>3</sub> sample such that no further observations could be made (Fig. 10).

# GROUP N (~27 300 CM<sup>-1</sup>)

In AmCl<sub>3</sub>, a single band is observed at 27 307 cm<sup>-1</sup> (Fig. 11), while Gruber and Conway<sup>12</sup> reported a single line at 27 328 cm<sup>-1</sup> which was  $\sigma$  polarized and split in a magnetic field. The results are consistent with assignment to a J=2 level in either  $D_{3h}$  or  $C_{3h}$  symmetry.

# GROUP O (~27 500 CM<sup>-1</sup>)

A relatively intense band without apparent structure is found in  $AmCl_3$  with center at 27 510 cm<sup>-1</sup> (Fig. 10). Preliminary calculation indicated a J=5 and a J=0level near this energy. In LaCl<sub>3</sub>: Am, Gruber and Conway<sup>12</sup> report three closely spaced lines of energy and polarization shown in Table II. Their results are consistent with a transition to a J=5 level in  $D_{3h}$  in symmetry.

The weak band at 27 747 cm<sup>-1</sup> may be classed as a vibronic overtone, but the isolated absorption at 27 948 cm<sup>-1</sup> seems to be too widely split from the 27 510-cm<sup>-1</sup> band to permit the same interpretation. Calculation places both  $J=0\rightarrow 0$  and  $J=0\rightarrow 3$  transitions in this range; the former is, of course, highly forbidden. A line was reported in II at 27 967 cm<sup>-1</sup> (Table II), which corresponds well with the isolated band at 27 948 cm<sup>-1</sup> in AmCl<sub>3</sub>, but a second  $\sigma$ -polarized component should be observed if the site symmetry were  $D_{3h}$ .

In AmBr<sub>3</sub> (Fig. 11) no assignments could be made to the group of numerous absorption maxima near 27 200  $cm^{-1}$ .

#### GROUP P (~28 000-29 000 CM<sup>-1</sup>)

Several relatively weak bands are found in this range in AmCl<sub>3</sub> (Fig 11), while Gruber and Conway<sup>12</sup> did not record lines in this region for LaCl<sub>3</sub>: Am. Of the levels calculated to occur in this energy range, all are forbidden to a first approximation so no electric-dipole intensity is computed. The more intense of these weak bands occurs at 28 678 cm<sup>-1</sup>, which corresponds to the predicted energy of the  ${}^7F_0' \rightarrow {}^5H_7'$  transition.

The spectrum of AmBr<sub>5</sub> in this region is complex and no interpretation can be offered.

## GROUP Q (~29 000-30 000 CM<sup>-1</sup>)

A strong band in AmCl<sub>3</sub> centered at 29 554  $\rm cm^{-1}$ (Fig. 12) correlates well with three lines observed in LaCl<sub>3</sub>:Am, as shown in Table II. A relatively intense transition to a J = 6 level is predicted at this energy, and the polarization of the lines in II would be consistent with the prediction if the site symmetry were  $D_{3h}$ .

The distinct band at 29 270 cm<sup>-1</sup> in AmCl<sub>3</sub> is then identified with a J = 4 level, whereas two lines are found in II (Table II). The bands at 29 868 and 29 985  $cm^{-1}$ are in good agreement with energies calculated for transitions to a J=5 and J=4 level, respectively. As was the case in Group P, the corresponding structure in AmBr<sub>3</sub> (Fig. 12) is comprised of numerous closely spaced bands, and no interpretation can be given.

Several additional assignments were made to the spectrum of  $AmCl_3$  at >30 000 cm<sup>-1</sup> as shown in Table II. For every group of lines reported for LaCl<sub>3</sub>: Am an absorption band was observed in AmCl<sub>3</sub>; however, only in the case of the group at  $\sim$ 33 400 cm<sup>-1</sup> did the number and polarization of lines at the corresponding energy in II constitute a confirmation of the assignment.

In this case the indicated site symmetry was  $D_{3h}$ . In other cases the number of lines reported was smaller than would have been expected for this transition in either  $D_{3h}$  or  $C_{3h}$  site symmetry.

# INTENSITY CONSIDERATIONS

As was pointed out earlier in this paper, intensity calculations based upon preliminary energy parameters were carried out and used as a qualitative aid in making or confirming some assignments. The theory of intensities of  $f^N$  transitions was used here in the form derived by Judd.<sup>24</sup> In this treatment the transitions, which are forbidden by a pure electric-dipole mechanism, can occur weakly because of the mixing into the  $f^N$  configuration of excited states of different parity via the oddparity components of the crystalline potential. In this general framework, a quantitative study of intensities for a series of halides might indicate whether configuration mixing within the metal ion is more important to the intensity than electron-transfer states involving the ligands.

The expression for the intensity of a transition may be written in the form<sup>25</sup>

$$P = \sum_{\lambda=2,4,6} \Im_{\lambda} \sigma(\psi J \mid\mid U^{(\lambda)} \mid\mid \psi' J')^2, \qquad (1)$$

where P, the oscillator strength of a transition between the levels  $\psi J$  and  $\psi' J'$  separated by  $\sigma(\text{cm}^{-1})$ , is related to the square of the matrix elements of the unit tensor operators  $\mathbf{U}^{(\lambda)}$  connecting the initial and final states via three quantities  $\Im_{\lambda}$ . Further, the three terms of (1) for  $f^6$  reduce to a single term with  $\lambda$  equal to the J value of the excited level. In the absence of J mixing the relation |J-J'| < 6 would hold and transitions from the

 <sup>&</sup>lt;sup>24</sup> B. R. Judd, Phys. Rev. **127**, 750 (1962).
 <sup>25</sup> W. T. Carnall, P. R. Fields, and B. G. Wybourne, J. Chem. Phys. 42, 3797 (1965).

ground (J=0) level occur only to even J levels. The appearance of transitions to odd-J' levels is, therefore, ascribed to J mixing. However, it remains to examine the extent of quantitative correlation between calculated and observed intensities of transitions to even-J-levels.

Because of the nature of the samples examined, experimental oscillator strengths could not be determined. We have, therefore, measured the areas of different absorption bands of the same sample examined at a given temperature and used this data as a basis for comparison. Calculated values of the quantities  $\sigma(\psi J \parallel U^{(\lambda)} \parallel \psi' J')^2$  were computed from the electrostatic and spin-orbit parameters which gave the best fit to the experimental energy levels for AmCl<sub>3</sub>. The results are given in Table II.

Since the quantity  $\sigma(\psi J \parallel U^{(\lambda)} \parallel \psi' J')^2$  is proportional to P, then it should also be proportional to the measured band area for different excited levels with the same J value.

Inspection of the appropriate columns of Table II shows that for J=2 levels of AmCl<sub>3</sub>, the greater the energy of the transition, the more the theory tends to underestimate the observed intensities. The same applies to J=4 levels. The agreement is quite good for the two contiguous J=6 levels, probably because they are not widely separated in energy and because the overlap from other levels is unlikely. Certainly the theory correctly predicts the most intense transitions. The partial results seem to indicate that this simplified model for the intensities gives a qualitative correlation of the intensities in AmCl<sub>3</sub>, but that the greater the energy of the excited levels, the less likely it is to find a consistent quantitative fit of the observed intensities. This suggests, in the framework of the theory used, that the mixing states of opposite parity are located at energies very close to the energy of the  $5f^6 \rightarrow 5f^6$  transitions. We shall briefly return to this question after considering the behavior of AmBr<sub>3</sub> and AmI<sub>3</sub>.

It is also assumed<sup>24</sup> that all components of the ground level are equally likely to be occupied. Normally, this basic assumption would exclude application of Expression (1) to low-temperature spectra, but in Am(III)the ground term is degenerate since it is a J=0 level.

Some interesting conclusions can be drawn from a comparison of the intensities of corresponding line groups in AmBr<sub>3</sub> and AmI<sub>3</sub>. The  ${}^7F_0' \rightarrow {}^7F_2'$  absorption in AmI<sub>3</sub> is more intense by roughly 50 times than the bromide absorption, while the intensities of the three absorptions to  ${}^{7}F_{3,4,5}'$  are quite similar in both systems. This points to a typical hypersensitivity effect in AmI<sub>3</sub>.

Another effect relates to the intensity ratios of transitions to odd-J and even-J excited levels. In the chloride the transition to  ${}^{7}F_{3}{}'$  is an order of magnitude weaker than that to  ${}^7F_2'$ . The same is true of the transition to  ${}^{7}F_{5}$  when compared to that to  ${}^{7}F_{4}$ . This is no longer true for AmBr<sub>3</sub> and AmI<sub>3</sub>. The transition to  ${}^7F_5'$  is comparable in intensity to that to  ${}^7F_4$ .

AmI<sub>3</sub> at  $\sim 21500$  cm<sup>-1</sup>, and this again involves J = $0 \rightarrow J = 2$  (this will be discussed below).

The two remaining transitions occurring in AmI<sub>3</sub> before the onset of the absorption edge are an order of magnitude larger than would be expected on the basis of the intensity predictions. On the whole it appears that the theory, while useful in the case of AmCl<sub>3</sub>, is in poorer agreement with the observations in AmBr<sub>3</sub> and  $AmI_3$ . The apparent relative increase in the intensity of vibronic transitions in the latter may in part account for the lack of agreement. On the other hand, electrontransfer states will rapidly approach in energy the  $5f^5$ configuration in the halide series from chlorides to iodides. The model of an isolated 5f<sup>6</sup> or 5f<sup>5</sup>6d configuration will progressively lose its validlty, and a molecularorbital description of the system will become pertinent.

#### HYPERSENSITIVITY

Hypersensitive effects have been found associated with transitions where  $\Delta J = 2$ ,  $\Delta L = 2$ , and  $\Delta S = 0.26$  Two hypersensitive transitions observed in AmI<sub>3</sub> are consistent with these selection rules. A possible hypersensitive transition predicted to occur at  $\sim 27~000~{\rm cm^{-1}}$  in AmI<sub>3</sub> could not be observed because of the absorption edge at  $\sim 25\ 500\ {\rm cm}^{-1}$ .

The assignments of Table I and II imply that the  $\Delta J = 2$  transitions at  $\sim 21\ 000\ {\rm cm}^{-1}$  in AmI<sub>3</sub> are essentially equally hypersensitive. On the basis of the composition of  ${}^{5}D_{2}{}'$  and  ${}^{5}G_{2}{}'$  and also of  ${}^{7}F_{0}{}'$ , if we assume the validity of the selection rule  $\Delta L = 2$ , then only the J=2 level with a large percentage of <sup>5</sup>G character should show hypersensitivity. This is level  ${}^{5}G_{2}'$ , which is predicted to have somewhat higher energy than  ${}^{5}D_{2}'$ . An alternative argument would ascribe less importance to the possible  $\Delta L = 2$  selection rule for hypersensitive transitions and place  ${}^{5}G_{2}'$  at 21 645 and  ${}^{5}D_{2}'$  at 21 370 cm<sup>-1</sup>, respectively. However, in this case there would be essentially no shift in the energy of these bands in AmI<sub>3</sub> vs AmBr<sub>3</sub>, which is unlikely. Present evidence seems more consistent with the assumption that  $\Delta L = 2$ is a valid selection rule for hypersensitive transitions.

Hypersensitivity has been reported for many lanthanide systems, although it has not previously been clearly identified in the case of trivalent actinides. The most recent explanation of the occurrence of hypersensitivity is based on the symmetry argument that the effect is connected with the presence of nonvanishing  $A_{1^0}$  terms in the crystalline potential.<sup>27</sup> The  $C_{3h}$  (or  $D_{3h}$ ) site symmetry<sup>28,29</sup> in AmCl<sub>3</sub> does not allow such terms. The Cmcm- $D_{2h}^{17}$  space group of AmBr<sub>3</sub>, where the site symmetry for Am is given<sup>30</sup> as  $C_{2\nu}$ , would allow hypersensitive transitions, but no such effect was observed.

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 <sup>28</sup> J. Fuger, J. Inorg. Nucl. Chem. 28, 3066 (1966).
 <sup>29</sup> L. B. Asprey, T. K. Keenan, and F. H. Kruse, Inorg. Chem. 4,985 (1965). <sup>30</sup> J. D. Forrester, A. Zalkin, D. H. Templeton, and J. C. Wall-

A second hypersensitive transition appears to occur in

The appropriate transitions do show hypersensitivity in AmI<sub>3</sub>, where the space group<sup>29</sup> is  $R\bar{3}-C_{3i}^2$ .

The observations by Ryan and Jørgensen<sup>31</sup> on octahedrally coordinated rare-earth halides are also relevant to the discussion of the observed hypersensitivity in AmI<sub>3</sub>. These authors found experimentally in such systems that the values of molar absorptivities for the  $4f^N$  transitions are lower by about an order of magnitude than the values found in the more familiar lanthanide systems. The spectra in these halide complexes are mainly vibronic as one would expect for an  $f^N$  ion in a site possessing, to a great approximation, a center of inversion. The interesting point is that amongst the transitions in these complexes, there are some that have molar absorptivities larger by an order of magnitued than those for the remaining transitions. This is a typical hypersensitivity effect.

We may draw the following correlation in the case of the americium halides. In AmCl<sub>3</sub>, there is ninecoordination of chloride ions about the metal ion. In AmBr<sub>3</sub> eight ions are coordinated to the Am(III) ion. Neither of these systems exhibit hypersensitivity. Americium tri-iodide exhibits the BiI<sub>3</sub> structure where the metal ion is coordinated by only six iodide ions located at the vertices of a nearly perfect octahedron. This more compressed structure, as was the case with the octahedral lanthanide halides, may be responsible for the observed hypersensitivity. Thus, one might argue that the extent of electronic cloud overlap of  $4f^N$  ions or  $5f^N$  ions with the ligands is the dominant factor responsible for hypersensitivity. The symmetry condition for hypersensitivity would thus appear to be a necessary condition but not a sufficient one.

#### CONCLUDING COMMENTS

The observed nephelauxetic behavior and the observed hypersensitivity effects in americium halides are another indication of the close similarity in the properties of  $4f^N$  and  $5f^N$  systems.

The theory of intensities for  $5f^N$  systems gives a fair rationalization of the observed relative intensities in AmCl<sub>2</sub>, although the agreement is less satisfactory for the two remaining halides.

Tentative identifications based on intensity considerations and experimental results for Am(III) in LaCl<sub>3</sub> have been proposed for many of the higher-energy excited levels of Am(III). Further work with crystal spectra will be required to establish the consistency of these assignments. The energy-level parameters obtained by fitting to the observed energy-level scheme indicate that configuration interaction is much the same magnitude as that found in the  $4f^N$  series, but it should also be emphasized that other parameter sets with slightly different values of  $\alpha$ ,  $\beta$ , and  $\gamma$  will also give a satisfactory fit to the observed levels at this stage. Additional experimentally established assignments are required before the parameters can be determined more precisely.

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