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ABSTRACT

The absorption and self-luminescence spectra of $Cf^{+3}(5f^9)$ in $LaCl_3$ has been observed between 3000A and 8500A. Several of the observed groupings indicate a small crystal-field splitting compared with the spin-orbit splitting. As the basis for a tentative assignment of the reported spectra, a perturbation calculation was made on the LSJ levels of the ground multiplet, ^6H_J, where $^6H_{15/2}$ is the ground level. If we assume $\zeta = 4000\ cm^{-1}$ and $F_2 = 300\ cm^{-1}$ for $Cf^{+3}(5f^9)$, we obtain for the lowest levels a theoretical energy spectrum in reasonable agreement with that observed.

ABSORPTION AND SELF-LUMINESCENCE SPECTRA OF $Cf^{+3}(5\underline{f}^9)$*

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INTRODUCTION

Since the discovery of element 98, californium, in 1950 by Thompson, Street, Ghiorso, and Seaborg,[1] studies on certain physical properties of Cf^{+3} by Cunningham and Wallmann[2] indicate that the +3 ion is similar to the rare earth analog, $Dy^{+3}(4\underline{f}^9)$. Cunningham has observed part of the absorption spectrum of $Cf^{+3}(5\underline{f}^9)$ on a Dowex-50 ion-exchange bead[2] and in an aqueous acid solution.[3] Very weak absorption peaks are observed at 7800 and 8320A in solution, and at 5750A on the bead.

The results we report in this paper tend to confirm these absorption features. In addition, several sharp but very weak absorption lines are observed in the ultraviolet region of the spectrum. As a result of these studies, we believe that the molar extinction coefficients of Cf^{+3} are in general between 1 and 10 -- a range quite similar to Dy^{+3}.

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CALIFORNIUM PURIFICATION

The major portion of californium (consisting of the isotopes Cf^{249}, ~10%; Cf^{250}, ~50%; and Cf^{252}, ~40%) used in our studies was isolated from the capture and fission products produced by a series of long neutron irradiations of Ur^{242}. After the initial separations, curium was removed by a series of column elutions from Dowex 50, 12% DVB, resin at 87°C with ammonium α-hydroxy-isobutyrate.[4] Berkelium was separated either during this ion-exchange procedure or by extraction of Bk^{+4} with di-iso-octyl ortho phosphoric acid.[5] Plutonium, lanthanum, and residual rare earths were separated from the combined californium fractions by a combination of ion-exchange methods.[6] Final purification consisted of iodate, hydroxide, and oxalate precipitations followed by elution of the adsorbed californium with 6M HCl from a 2-mm by 4-cm Dowex 50 colloidal resin bed. To provide the necessary crystal matrix, approximately 1 mg of 99.997% pure La_2O_3 (Lindsey Chemical Co.) was dissolved in approximately 0.3 ml of eluate.

PREPARATION OF $CfCl_3$-$LaCl_3$ CRYSTALS

The solution containing Cf^{+3} and La^{+3} in chloride form was transferred to a 6-mm quartz tube and slowly evaporated to dryness. A stream of dry hydrogen chloride was passed over the material at 400°C to produce the anhydrous chlorides. As a final step in purification, the anhydrous chlorides were sublimed under vacuum, and the sublimate collected in a portion of the quartz tube that could be sealed off and removed from the vacuum line. The evacuated quartz tube containing the $CfCl_3$-$LaCl_3$ was passed through a crystal-growing furnace.[7]

Because the total volume of the sample was less than 0.5 mm^3, the

crystal was regrown in a 0.4-mm-diam. quartz capillary tube attached to a joint having a 90-deg bend near the opening. The sample from the 6-mm tube was transferred in a dry box to the capillary tube, and the latter attached to a vacuum line. The material was contained in the 90-deg bend where complete outgassing was possible. The capillary tube was then rotated so that the sample fell to the bottom. The tube was then sealed under vacuum, and slowly lowered through a crystal growing furnace.[7]

OBSERVATIONS AND CONCLUSIONS

The self-luminescence and absorption spectra of Cf^{+3} in $LaCl_3$ were photographed on a Hilger f/4 quartz spectrograph and a Jarrell Ash f/6 grating spectrograph. The spectra could be photographed in a matter of several hours, although exposures as long as 90 hr were necessary in order to observe several weak satellite lines associated with certain strong-resonance emission lines. A low-pressure Hg lamp provided a standard reference spectrum. With the exception of two groupings in the infrared, the luminescence spectrum was observed with both instruments.

As a result of intense radioactivity, the crystals blackened with time because of the formation of color centers. In order to recover the optical quality of a crystal, it was necessary to anneal it at 110°C for several hours.

A strong continuum is observed extending from 3000 to 5000A. Superimposed on this continuum and extending beyond it into the infrared are the distinct peaks of Cf^{+3}. The continuum is associated with the bremsstrahlung radiation observed in the self-luminescence spectrum of various radioactive ions.[8] In addition, six features are observed in the spectrum corresponding to absorption groupings. In Table 1 we list the wavelengths of the observed groupings and note in particular that groups at 3504, 4004, and 5940A show

structure. Such structure indicates a small crystal-field splitting compared with the spin-orbit splitting.

Table 1. Absorption and self-luminescence spectra of Cf^{+3}

Number	Wavelength in air (A)	Wavenumbers in vacuum
1	3114[a]	32,100
2	3448[b]	28,990
3	3504[b]	28,530
4	3541[b]	28,230
5	3587[b]	27,870
6	4004[a,c]	24,970
7	4102[a,b]	24,370
8	4361[a]	22,920
9	4583[a]	21,810
10	5006[a]	19,970
11	5320[a]	18,790
12	5750[d]	17,390
13	5940[a]	16,830
14	6500[a]	15,380
15	7200[a]	13,890
16	7800[e]	12,820
17	8320[e]	12,020
18	8400[a]	11,900

a. Luminescence spectrum of Cf^{+3} in $LaCl_3$.

b. Absorption spectrum of Cf^{+3} in $LaCl_3$.

c. This is close to a Cm^{+3} fluorescence peak, but the separation chemistry should have removed Cm^{+3}. For that reason we believe this peak is due to Cf^{+3}.

d. Observed on ion-exchange bead.[2] We believe this peak corresponds to the 5940A peak of Cf^{+3} in $LaCl_3$.

e. Observed in solution absorption spectra.[3]

As the basis for a tentative assignment of the reported energy spectrum, a perturbation calculation was made that considers the effect of the ^4G_J, ^4H_J, and ^4I_J levels upon the ground multiplet, ^6H_J. The general treatment is based on the method of evaluating the spin-orbit matrix elements given by Judd.[9] If we assume $\zeta = 4000\ cm^{-1}$ and $F_2 = 300\ cm^{-1}$ for $Cf^{+3}(5\underline{f}^9)$, and assume further that the observed absorption spectrum in the visible and ultraviolet corresponds to several of the previously mentioned excited multiplets, we obtain a calculated energy spectrum for the lowest levels of the ground multiplet, ^6H_J, that is in reasonable agreement with the observed energy spectrum reported in Fig. 1. Assignments are based on the parent LSJ levels. There is no question that intermediate coupling effects are important in the ground multiplet. However, the actual composition of the states is not known at present.

Because of the small quantity of material used and the low molar extinction coefficients, much of the expected absorption spectrum of Cf^{+3} has not yet been observed. More definitive assignments must await polarization and Zeeman studies on larger crystals containing larger quantities of the less radioactive isotope, Cf^{249}.

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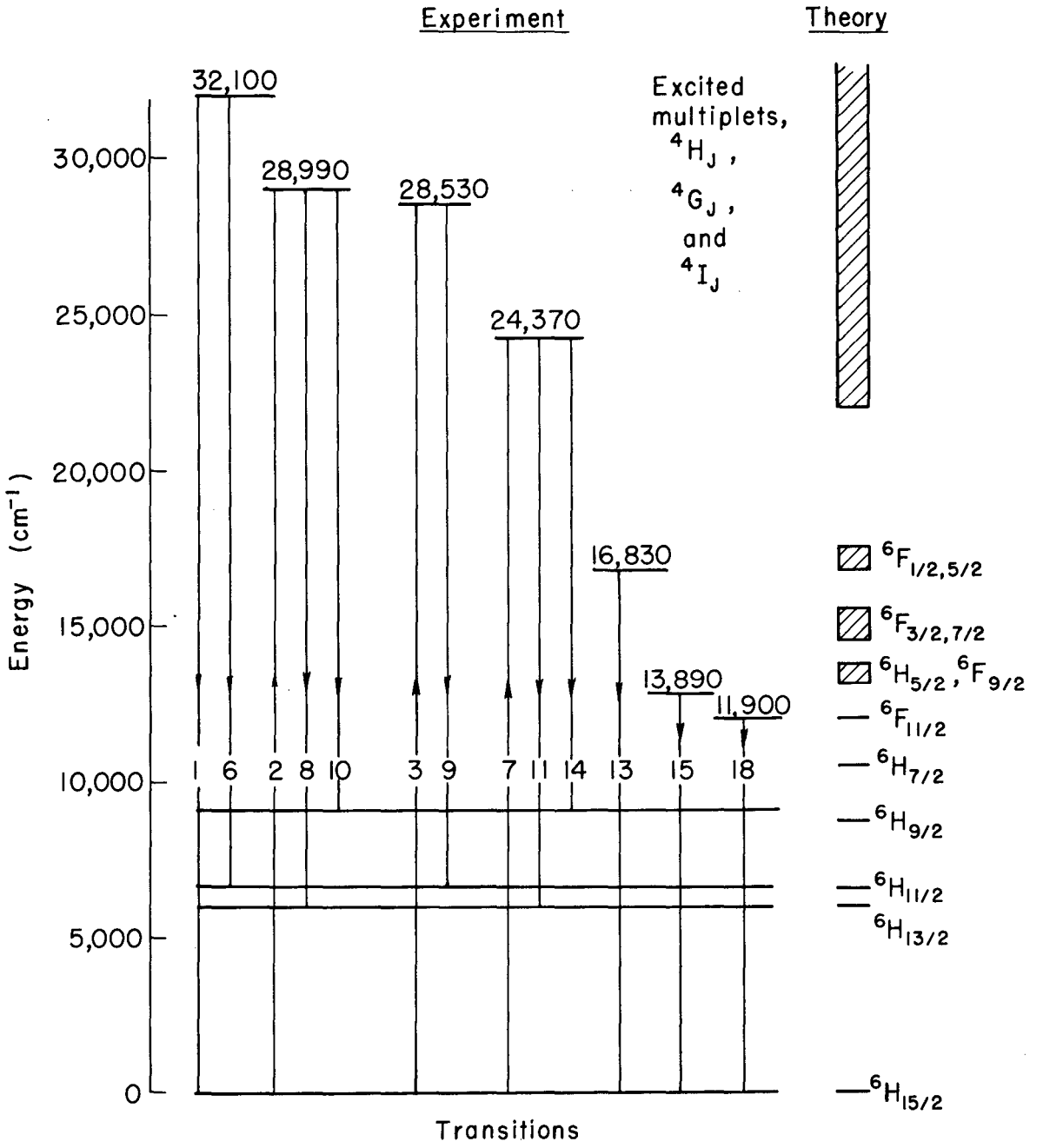

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Fig. 1. Suggested energy-level scheme for $Cf^{+3}(5f^9)$ in $LaCl_3$. On the left is the observed energy spectrum, and on the right, the results from perturbation theory, where $F_2(5f^9) = 300$ cm^{-1} and $\zeta = 4000$ cm^{-1}. The numbered transitions correspond to the observed absorption and luminescence features reported in Table I.

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