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Authors

Mclaughlin, R.

White, R.

Edelstein, N.

et al.

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University of California
Ernest O. Lawrence
Radiation Laboratory

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OPTICAL SPECTRA OF Pu IN CaF₂*

R. McLaughlin, R. White,† N. Edelstein, and John G. Conway

Lawrence Radiation Laboratory
University of California
Berkeley, California

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ABSTRACT

The optical spectra of Pu³⁺, Pu⁴⁺, and color centers, in CaF₂ have been measured. Tetravalent Pu and the color centers are formed in the crystal as the result of the decay of the Pu nucleus. Fluorescence spectra of Pu³⁺ and Pu⁴⁺ are also obtained.

INTRODUCTION

In the lanthanide series of the periodic table all the elements have been stabilized in the divalent state in CaF_2 crystals.¹ We have recently shown that this is also true for Am doped CaF_2 .² We have tried to stabilize other actinides in the divalent state and in this paper present our results on the study of the optical spectra of Pu doped CaF_2 crystals.

EXPERIMENTAL

Single crystals of CaF_2 each containing 0.1 - 0.2 wt % of ^{239}Pu ($t_{1/2} = 24360$ years) or ^{238}Pu ($t_{1/2} = 89$ years) were grown as described previously.² Absorption spectra were obtained with a Jarrell-Ash Model 75, F/6 spectrograph and a Cary Model 14 spectrophotometer. Fluorescent spectra were obtained with a Jarrell-Ash 0.25 Meter Ebert monochromator from which the slits had been removed. The sample was placed at the entrance slit and was excited by the radiation from a 1000 watt A-H6 Hg lamp filtered through a CuCl_2 solution. Crude thermoluminescent data were obtained by placing the sample surrounded by a nichrome wire heater coil at the slit of the monochromator and recording the output of the grating scan with a photomultiplier as the

sample temperature was raised. Since the intensity of the emission varied as the temperature changed it was difficult to determine if emission peaks occurred because of the wavelength scan or because of the temperature change. By repeating the process several times reliable data were obtained.

RESULTS AND DISCUSSION

The crystals were colorless or light blue when removed from the furnace but turned to a deep blue color after a period of time. It required several months for a marked color change to occur in the ^{239}Pu doped crystals but only a day or so for those crystals containing ^{238}Pu . This coloration was caused by the radiation damage of the crystals due to the bombardment by alpha particles emitted during nuclear decay and will be discussed later.

Previous work on lanthanides and on Am doped CaF_2 suggested that under the conditions which the crystals were grown Pu should be incorporated in the crystal in the trivalent state. Lämmermann and Conway³ found three groups of sharp lines which shifted only slightly between Pu^{3+} in $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and Pu^{3+} in LaCl_3 . These lines were found (slightly shifted) in Pu in CaF_2 as shown in Table I. This observation confirmed the presence of Pu^{3+} when the crystals were originally grown.

Two types of spectral features grew in as the radiation damage continued; broad bands of $\sim 100\text{\AA}$ half width, and sharp lines of $\sim 1\text{\AA}$ half width. The wavelengths of these features are listed in Table II. The ground configuration of divalent Pu would most likely be f^6 . An attempt was made to predict this

spectrum by interpolation between the energy levels of neutral Pu (configuration $f^6 s^2$), Am^{3+} (configuration f^6)⁴ and Cm^{4+} (configuration f^6).⁵ However no correlation was found between the observed and the predicted spectrum. Attempts were then made to correlate the observed spectrum with the solution spectrum of tetravalent Pu.⁶ This correlation was suggestive but not certain. In general the spectra of actinides are more sensitive to their environment than the spectra of lanthanides; hence this kind of comparison is less positive.

The issue was resolved by obtaining the spectrum of Pu^{4+} in a CaF_2 matrix. This was accomplished by coprecipitating Pu^{4+} and CaF_2 from an HCl solution by the addition of concentrated HF. The Pu was kept in the tetravalent state by the addition of NaNO_2 prior to precipitation.⁷ The precipitate was dried with a heat lamp, mullied with mineral oil, and pressed between two quartz plates in order to obtain the spectrum. The lines of the mull were much broader than the lines of the crystal. This is believed to be due to the presence of water incorporated into the precipitate. All spectra were obtained with samples immersed in liquid nitrogen. The correspondence between the spectra of the crystal and the mull is shown in Fig. 1. The broad band features from the crystal are not included in this figure because the lack of correspondence between the mull spectrum and crystal broad band spectrum indicated that these features were not associated with the Pu^{4+} ion, but were probably due to color centers. The two effects which cause the change in color of these crystals are a) the change in valence of the Pu ion, and b) the production of color centers.

In the course of these investigations it was noted that the ^{238}Pu doped crystal took on a different shade of blue coloration if radiation damage occurred

at liquid nitrogen temperature. Further examination revealed that the sharp lines did not grow in at 77°K. Hence this new color was caused by the presence of only those features labeled as broad bands in Table II whereas in the room temperature damaged crystal both the sharp Pu⁴⁺ lines and the broad bands contributed to the color.

This observation implies that it is necessary for an electron deficient center to diffuse to the vicinity of the Pu ion in order for conversion from the trivalent to the tetravalent state to occur. The mobility of this center is greatly reduced at 77°K. Such electron traps have been proposed previously.⁸

After a few days of radiation damage at room temperature, the intensities of the Pu⁴⁺ absorption lines were greater than that of the Pu³⁺ lines in the ²³⁸Pu doped crystal. However the intensity of the Pu³⁺ lines had only decreased slightly. From this observation it is apparent that the absorption coefficients for Pu⁴⁺ must be greater than for the Pu³⁺ ions. Total conversion of Pu³⁺ to Pu⁴⁺ did not occur. In light of earlier work on lanthanide ions in CaF₂ crystals it is probable that only Pu³⁺ ions in certain symmetry sites were oxidized to the higher valence state.

Since most lanthanide doped CaF₂ crystals fluoresce when irradiated with ultra violet light, this effect was sought in these Pu crystals. No visible light emission could be detected by the eye, but an infra-red peak was recorded at 1.78 μ in the Pu³⁺ crystal. In the radiation damaged crystal there was an additional peak at 1.93 μ which disappeared on heating. This feature was assigned to Pu⁴⁺. The width of the emission lines was determined by the slit width of the spectrometer.

This tendency to fluoresce in the infrared and not in the visible is demonstrated by U^{3+} and Np^{3+} doped CaF_2 crystals as well as in Pu^{3+} crystals. It seems likely that the greater crystal field splitting of the CaF_2 lattice renders de-excitation by non-radiative processes more probable because of the high density of J levels in the visible region.⁹ In the infrared region J levels are well separated and de-excitation by fluorescent processes is found.

Even though visible fluorescence could not be observed with external excitation, the radiation damaged crystals did emit blue light upon heating. Crude spectral measurements indicated this thermoluminescence was most intense at 4800 Å and 5800 Å. Previous results with Am and Cm doped CaF_2 crystals¹⁰ would indicate that the thermoluminescence and fluorescence of the Pu crystals is characteristic of the Pu^{3+} ion. It is likely that the 4800 Å and 5800 Å peaks could be correlated to 5200 Å and 6200 Å fluorescent peaks reported for Pu^{3+} in $LaCl_3$.¹¹

It is interesting to compare the positions of levels due to configuration f^4 in a trivalent ion and in a tetravalent ion. For this purpose we used data for Np^{3+} .¹² The comparison is difficult for all but the lowest levels since the higher levels are too dense to correlate an observed absorption line with a known level. We find for the three lowest levels above ground a constant shift of $\sim 1700\text{ cm}^{-1}$ to higher energy of Pu^{4+} compared to Np^{3+} . This shift occurs because the larger nuclear charge in the tetravalent ion causes the spin-orbit interactions and the interelectronic repulsions to be larger. The result is a general spreading out of levels.

SUMMARY

The optical spectrum of Pu^{3+} in CaF_2 has been measured. Formation of Pu^{4+} was found in these crystals as a consequence of the radioactive decay of the Pu nuclei. This growth of Pu^{4+} was temperature dependent. Color centers were also found in these crystals. Although there was no evidence for the formation of divalent Pu, we cannot definitely state that this oxidation state was not formed.

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Footnotes and References

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†NSF summer visitor — present address: Science Department, Clarksvilles Jr.-Sr. High School, Clarksvilles, Ind. 47131.

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Table I. Comparison of centers of groups of sharp lines of Pu³⁺.

	Center of group (cm ⁻¹)		
La(Pu)(C ₂ H ₅ SO ₄) ₃ · 9H ₂ O	19635	16014	14956
Ca(Pu)F ₂	19895	16411	15186
Difference	260	397	230

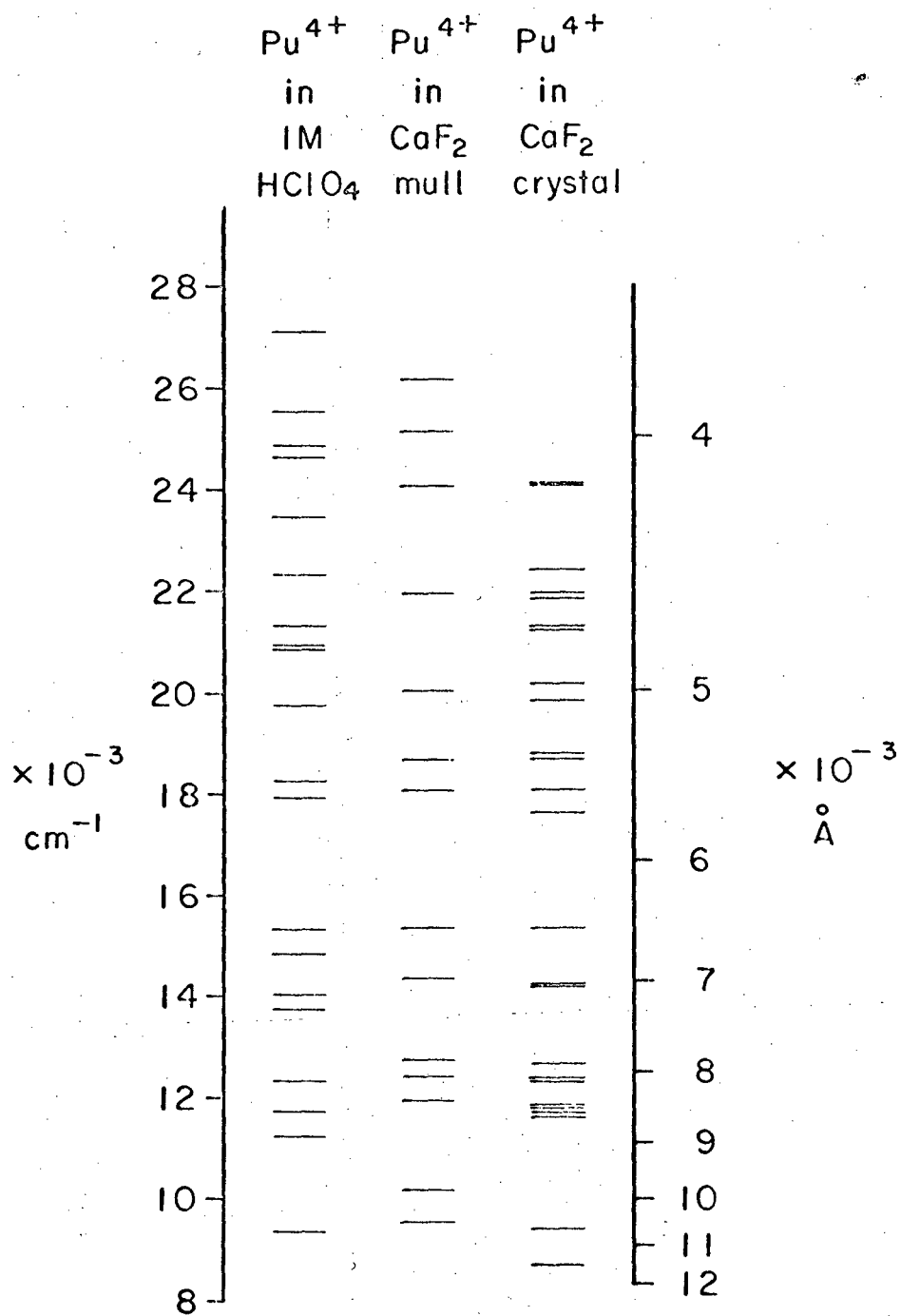
Table II. Lines which grow into Ca(Pu)F₂ crystal due to a radiation damage.

Wavelength (Å)	Wave number (cm ⁻¹)	Intensity ^a
Half width $\approx 1 \text{ \AA}$		
4149	24095	m
4151	24084	w
4154	24066	w
4463	22400	w
4554	21953	s
4559	21928	w
4584	21809	w
4693	21302	w
4712	21216	w
4955	20176	w
5040	19836	w
5323	18781	w
5349	18690	w
5537	18055	m
5674	17619	w
5676	17613	w
6518	15338	m
7006	14270	w
7021	14239	w
7889	12672	w
8088	12361	w

Table II. (Continued)

Wavelength (Å)	Wave number (cm^{-1})	Intensity ^a
Half width $\approx 1 \text{ \AA}$		
8093	12353	w
8099	12344	w
8431	11858	m
8447	11835	w
8527	11724	w
8608	11614	w
10600	9431	
11440	8739	
1.85 μ	5400	
Half width $\approx 100 \text{ \AA}$		
5998	16670	
6328	15800	
6576	15200	
8057	12400	

^as = strong, m = moderate, and w = weak.



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Fig. 1. Energy level diagram of Pu⁴⁺ in various solutions.

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