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IN SINGLE CRYSTALS

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ABSTRACT

The formation and stabilization of various oxidation states of actinide positive ions in  $\text{CaF}_2$  crystals is described. Paramagnetic resonance and optical spectra are reported for divalent Am and trivalent Cm in these crystals. Tetravalent Cm and Pu, formed as a consequence of the intense alpha radiation, are identified by their optical spectra.

## INTRODUCTION

Rare earth ions are stabilized in the divalent state in crystals of alkaline earth halides.<sup>(13)</sup> This oxidation state is usually formed by reduction of the trivalent rare earth ion to the divalent form by one of three methods, gamma irradiation of the crystals,<sup>(13)</sup> solid state electrolysis,<sup>(4)</sup> or alkaline earth metal reduction.<sup>(9)</sup> The last two techniques are more efficient since under some conditions all of the trivalent rare earth ions can be reduced. Recently we reported the stabilization of divalent Am in  $\text{CaF}_2$ , the first well characterized divalent actinide.<sup>(3)</sup> In this paper we will briefly review the Am work and summarize our further attempts to find other divalent actinides. We will also report on the paramagnetic resonance (PMR) spectra of  $\text{Cm}^{3+}$  in  $\text{CaF}_2$ .

Experimental

The actinide-doped single crystals of  $\text{CaF}_2$  were grown by the Bridgman-Stockbarger technique. A concentrated solution of the actinide in 10-50% of weak  $\text{HNO}_3$  solution was pipeted onto a powder of  $\text{CaF}_2$  containing 2 wt. %  $\text{PbF}_2$ , which had been placed in a carbon crucible. The crucible and sample were then placed in a furnace, melted under vacuum, and then the crucible was lowered slowly through the hot zone of the furnace. PMR measurements were taken at  $4.2^\circ\text{K}$  and  $1^\circ\text{K}$  at a frequency of approximately 9.0 Gc/sec with a superheterodyne spectrometer. Optical measurements were made at room temperature and  $77^\circ\text{K}$  with a Cary Model No. 14 spectrometer and a Jarrell-Ash F-6 spectrometer using photographic plates.

Results and Discussions

Am in  $\text{CaF}_2$ . Crystals grown with Am are light pink initially. On standing for periods of weeks to months they darken to a brown color. The initial absorption spectrum shows lines characteristic of trivalent Am, Figure 1b. As the

crystal darkens due to radiation damage, new broad bands grow in as shown in Figure 1a. Figure 1c shows the spectrum obtained from an electrolytically reduced crystal. The origin of these new broad bands is probably due to f to d transitions of divalent Am. The crystals which have darkened show at 4°K and 1°K a six line isotopic PMR spectrum which is assigned to the  $\Gamma_6$  crystal field state of the  $8S_{7/2} (f^7)$  electronic configuration of divalent Am in cubic symmetry. Since both  $^{241}\text{Am}$  and  $^{243}\text{Am}$  have nuclear spins of  $I=5/2$  the line is split into six hyperfine components. The measured parameters of the spin Hamiltonian

$$H = g\beta H \cdot S' + A I \cdot S'$$

for  $\text{Am}^{2+}$  in  $\text{CaF}_2$  are given in Table I. The  $g$  value calculated for the  $\Gamma_6$  crystal field state of  $\text{Am}^{2+}$  using wavefunctions given by Lea, Leask, and Wolf<sup>(11)</sup> and the Lande  $g$  value taken from atomic beam data on atomic Am<sup>(12)</sup> is 4.517. The agreement between experiment and theory is very satisfactory.

After the crystals have aged for several weeks or longer, on heating to about 500°C they emit an intense green thermoluminescence characteristic of trivalent Am in non cubic sites. Figure 2 shows the emission spectrum of this thermoluminescence photographed at 500°C and the absorption spectrum of trivalent Am taken at 77°K. There is a shift in the centers of the lines due to different crystal fields at the two temperatures but the emission is clearly from ions in sites that are the same as those which cause the absorption spectrum. This type of thermoluminescence has been observed in rare earth doped  $\text{CaF}_2$  and a reaction mechanism has been given.<sup>(8,14)</sup>

$\text{Cm}^{3+}$  in  $\text{CaF}_2$ . Crystals grown with Cm are initially pale yellow or almost colorless after annealing. Because of the damage due to the high radiation level they are rose colored after one hour. After 3-4 hours the color has changed to burgundy red, and in about 15 hours the crystals are coal black. At all temperatures

the characteristic orange glow of  $\text{Cm}^{3+}$  is present which is due to emission from crystal field levels of the first excited electronic state down to the ground electronic state. The change in color of the crystal is due to the growth of a broad absorption band centered at  $5000\text{\AA}$  with about a  $2000\text{\AA}$  half width. Besides this broad absorption band which grows in with time, there are a number of relatively sharp lines which start to appear after annealing. These lines have been assigned to  $\text{Cm}^{4+}$  in the  $\text{CaF}_2$  crystal. Figure 3 shows the energy level diagram of  $\text{Cm}^{3+}$  and  $\text{Cm}^{4+}$  in the  $\text{CaF}_2$  crystal. For comparison we show the data of Gruber and Conway on  $\text{Cm}^{3+}$  in  $\text{LaCl}_3$  (6) and the data obtained by Keenan on  $\text{CmF}_4$ . (7)

Trivalent rare earth or actinide ions can be incorporated in the alkaline earth halides in sites of various symmetries. Since the crystal as a whole must be electrically neutral, charge compensating ions must also be present. The arrangement of these charge compensating ions about the rare earth (or actinide) ion determines the symmetry site of the impurity ion and its crystal field splittings. The most common symmetry sites present in these types of crystals are cubic, tetragonal, and trigonal. (15) The sites present are dependent on the way the crystals are grown and annealed. (5) In our  $\text{Cm} - \text{CaF}_2$  crystals we find trivalent  $\text{Cm}$  in the cubic site and in two different trigonal sites.

Preliminary values of the  $g$  tensor in the two trigonal sites are given in Table II. Also included is the value for the cubic site. In all three sites the crystal field splitting is large and at  $4^\circ\text{K}$  and  $1^\circ\text{K}$  we see only resonance lines from the ground crystal field state. The  $g$  value for the cubic site is, within experimental error, the same as divalent  $\text{Am}$  in  $\text{CaF}_2$  and therefore the  $\Gamma_6$  crystal field state is the lowest for this ion also. This  $g$  value also agrees with the work of Abraham, Judd, and Wickman on  $\text{Cm}^{3+}$  in  $\text{LaCl}_3$ . (1)

The number of absorption lines we obtain from the  $\text{Cm}^{4+}$  depends on the temperature at which radiation damage takes place. If, after annealing, the



crystal is kept at room temperature more absorption lines are found than when the crystal is placed at 77°K. More diffusion of charge compensating ions takes place in the crystal at the higher temperature with the consequence that more symmetry sites appear.

Pu in CaF<sub>2</sub>. Crystals grown with <sup>239</sup>Pu are light blue in appearance and gradually change to a deeper blue in periods of months. Crystals with <sup>238</sup>Pu changed to a deep dark blue in a few days. Optical spectra of the trivalent <sup>239</sup>Pu - CaF<sub>2</sub> crystals shows three groups of sharp lines and a number of groups of diffuse lines. This result is similar to that of Lämmermann and Conway<sup>(10)</sup> who found in the spectra of trivalent Pu in La ethylsulfate only three groups of sharp lines. The center of the three groups of sharp lines of Pu in CaF<sub>2</sub> agree with the centers of the three sharp line groups in the ethylsulfate crystal within 300 cm<sup>-1</sup>. In the <sup>238</sup>Pu - CaF<sub>2</sub> crystal, two types of absorption lines appeared with time after annealing the crystal; broad bands of ~100Å half-width and sharp lines of ~1Å half-width. We have considered the sharp line spectrum separately from the other structure and assign it to Pu<sup>4+</sup> in the crystal.

Figure 4 shows an energy level diagram of Pu<sup>4+</sup> in various diluents. The first column is the data of Cohen<sup>(2)</sup> on Pu<sup>4+</sup> in 1 M HClO<sub>4</sub>. Because we felt the agreement with our data on the Pu<sup>4+</sup> in CaF<sub>2</sub> crystal (column 3 in Figure 3) was not conclusive, we coprecipitated approximately 10 wt. % Pu<sup>4+</sup> with CaF<sub>2</sub> and took the optical spectrum of the precipitate in a mineral oil mull. This data is shown in column 2. The agreement of the mull data with the crystal data is quite satisfactory. The broad bands are most likely due to color centers formed in the crystal or associated with Y<sup>3+</sup> impurities. However the broad bands formed in the <sup>238</sup>Pu - CaF<sub>2</sub> system show no correspondence with the broad band formed in the Cm-CaF<sub>2</sub> system.

If the  $^{238}\text{Pu} - \text{CaF}_2$  crystal after annealing is kept at  $77^\circ\text{K}$ , no sharp lines appear indicating that no  $\text{Pu}^{4+}$  is formed at this temperature. However the broad bands do appear which give the crystal a different shade of blue than that which appears at room temperature. Again this result must be due to the diffusion of various species which can or cannot take place in the crystal depending on the temperature.

#### CONCLUSION

Our results show that as expected Am is the actinide element which forms the divalent oxidation state most easily. In our attempts to form divalent Pu and Cm we found instead sharp line spectra due to the tetravalent state. Our experiments do not exclude the possibility that divalent ions of these elements are formed because we do not have an unambiguous method of detection. However in our attempts to make divalent ions we have found interesting solid state chemical effects due to the high level of radiation in the crystals.

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TABLE I

	$\text{Am}^{2+}$ in $\text{CaF}_2$	$S' = 1/2, I = 5/2$
	$g = 4.490 \pm .002$	
	$A \times 10^2 \text{ (cm}^{-1}\text{)}$	
$^{241}\text{Am}$	$1.837 \pm .002$	
$^{243}\text{Am}$	$1.821 \pm .002$	
	$\frac{A(^{241}\text{Am})}{A(^{243}\text{Am})} = 1.009 \pm .001$	

Spin-Hamiltonian parameters of  $\text{Am}^{2+}$  -  $\text{CaF}_2$ .

TABLE II

$\text{Cm}^{3+}$  in  $\text{CaF}_2$   $S' = 1/2$

Cubic Site

$$g = 4.492 \pm .002$$

Trigonal Site I

$$g_{\parallel} = 3.41 \pm .02 \quad g_{\perp} = 6.88 \pm .02$$

Trigonal Site II

$$g_{\parallel} = 2.69 \pm .02 \quad g_{\perp} = 5.91 \pm .02$$

Spin Hamiltonian parameters of  $\text{Cm}^{3+}$  -  $\text{CaF}_2$ .

FIGURE CAPTIONS

Figure 1

- 1a) Optical spectrum of a radiation reduced  $\text{Am}^{2+}$ - $\text{CaF}_2$  crystal.
- 1b) Optical spectrum of  $\text{Am}$  -  $\text{CaF}_2$  crystal after annealing.
- 1c) Optical spectrum of an electrolytically reduced  $\text{Am}^{2+}$ - $\text{CaF}_2$  crystal.

Figure 2

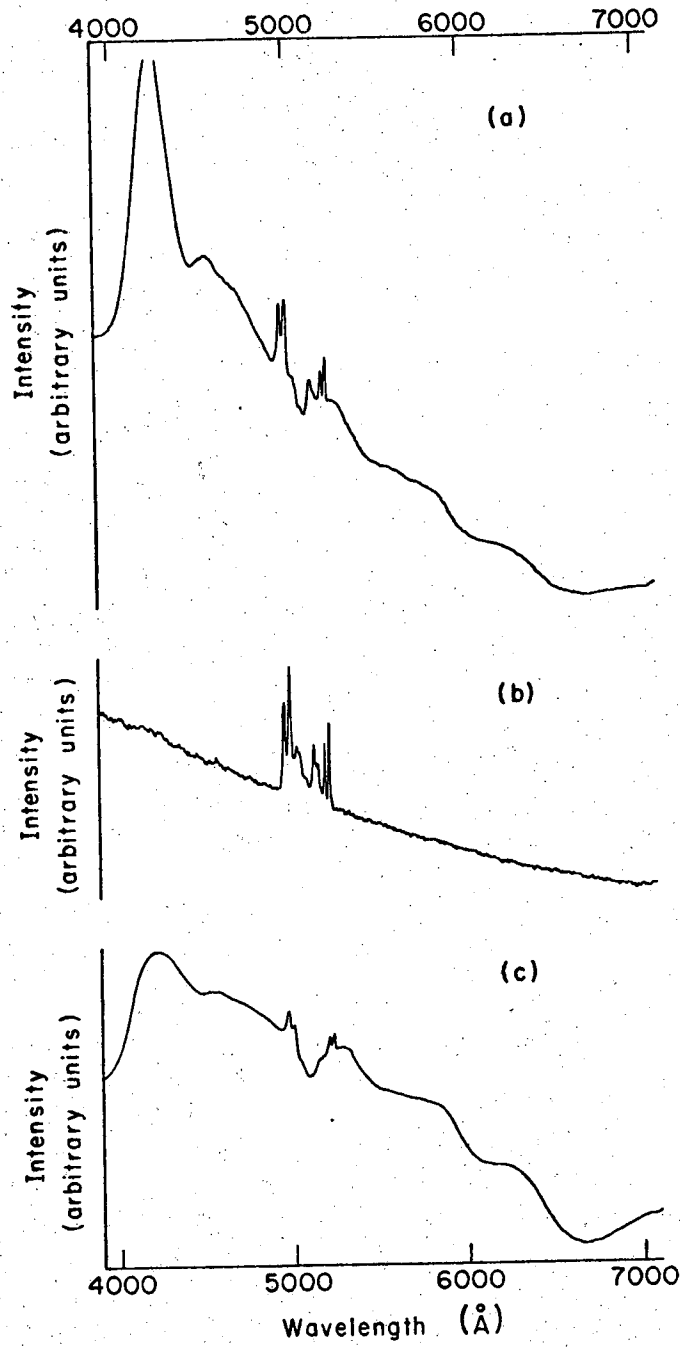
- Top - Emission spectrum of a radiation reduced  $\text{Am}^{2+}$ - $\text{CaF}_2$  crystal at  $\sim 500^\circ\text{C}$ .
- Bottom - Absorption spectrum of  $\text{Am}^{3+}$ - $\text{CaF}_2$  at  $77^\circ\text{K}$ .

Figure 3

Energy level diagram of  $\text{Cm}^{3+}$  and  $\text{Cm}^{4+}$  in various matrices.

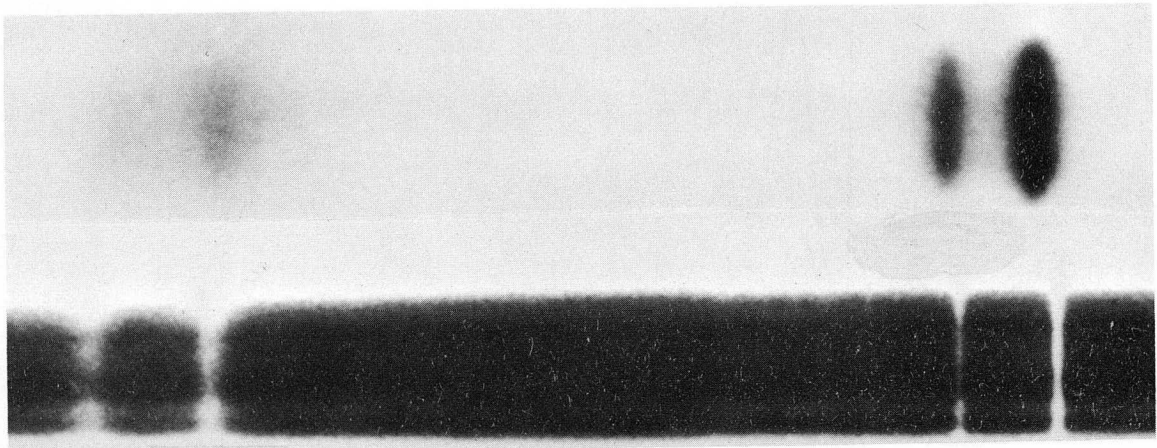
Figure 4

Energy level diagram of  $\text{Pu}^{4+}$  in various matrices.



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Fig. 1



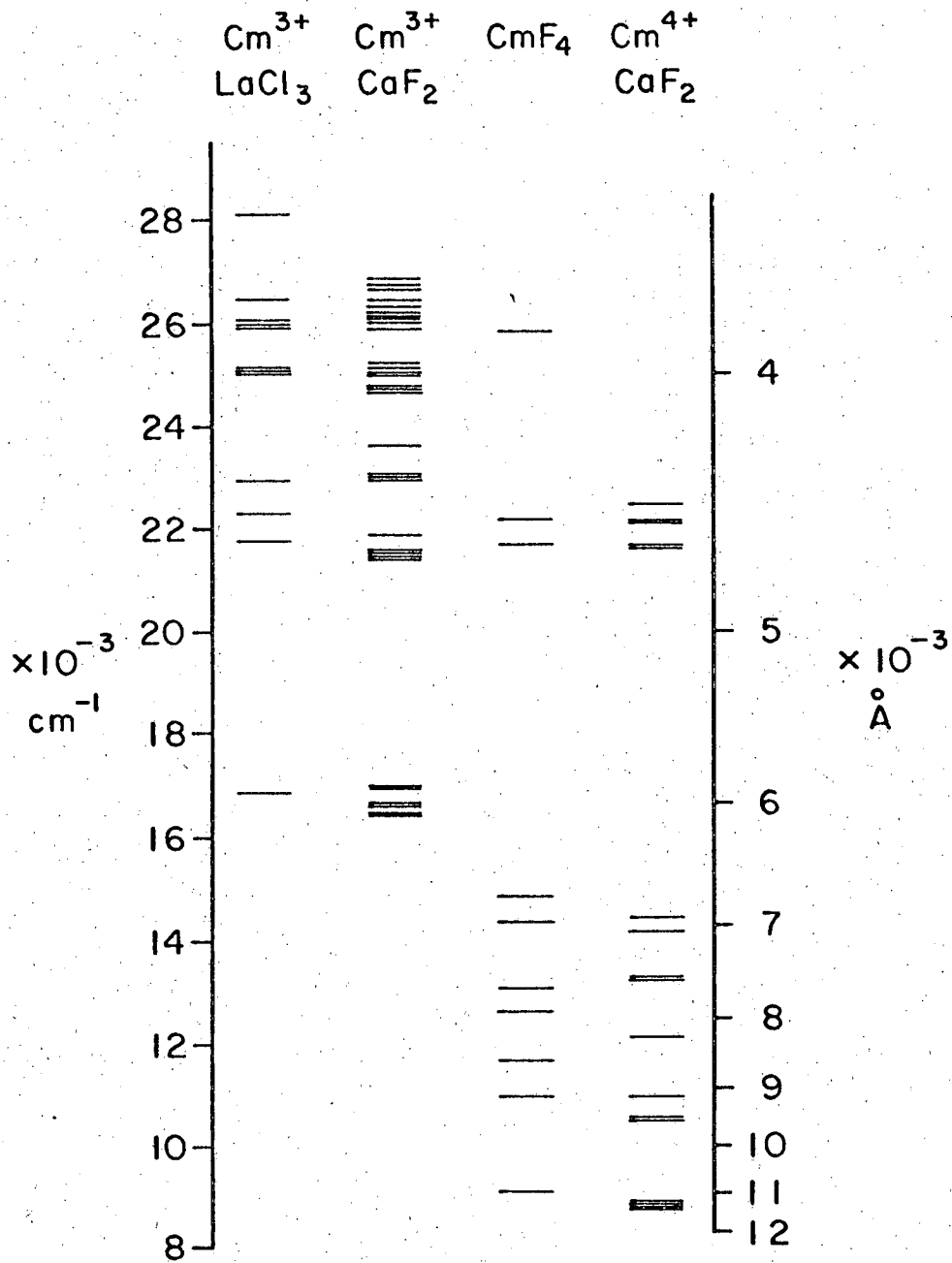
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9 9  
6 9  
1 6  
Å Å

5 5  
1 2  
9 2  
5 3  
Å Å

ZN-6000

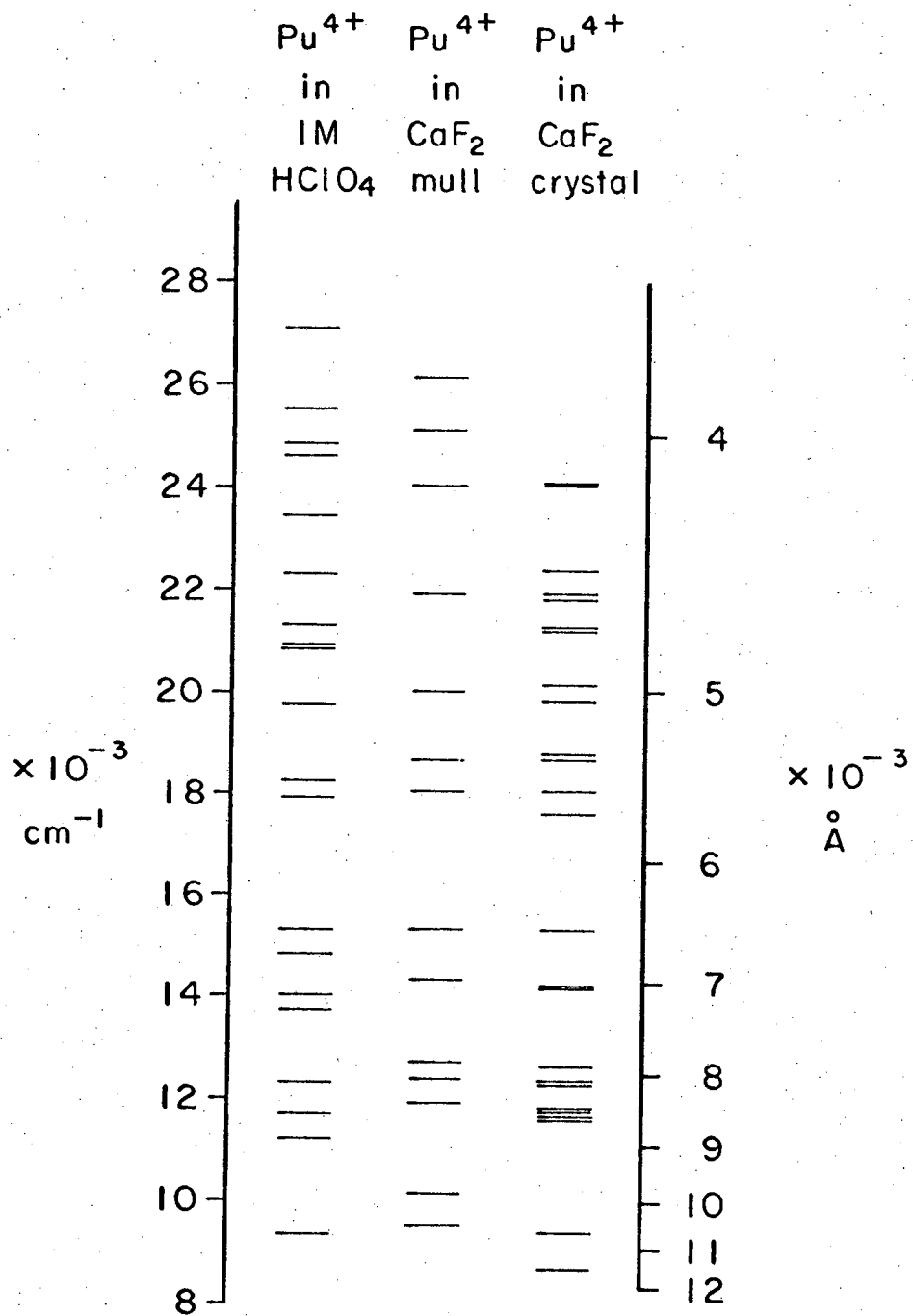
Fig. 1





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Fig. 3



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Fig. 4

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