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FORMATION AND CHARACTERIZATION OF DIVALENT EINSTEINIUM IN A CaF_2 CRYSTAL*

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Although no compounds of divalent actinides have been isolated, tracer chemistry experiments[1] and interpretation of charge transfer bands in the visible and UV spectral range[2] indicate that actinide elements with $Z > 97$ might form a chemically stable dipositive oxidation state. Dipositive states of the entire lanthanide series have been stabilized in crystals of CaF_2.[3] However, the only dipositive actinide ion positively identified as being stabilized in CaF_2 has been Am^{2+}.[4] We now report the identification by electron paramagnetic resonance of Es^{2+} ($Z = 99$) in CaF_2.

Powdered CaF_2 ($\sim$ 3mg) to which had been added 2 wt. % PbF_2 was placed in the center of a spectroscopic grade carbon rod in which a small hole had been drilled. Approximately 6 μg of purified $^{253}Es^{3+}$ ($t_{1/2}$ = 20.5 days) in a volume of $\sim$ 1 λ HCl[5] was pipeted onto the powder. The carbon rod was attached to two electrodes, the apparatus was evacuated, and current was passed through the rod until the CaF_2 powder was seen visually to coalesce. The current was immediately turned off, and after cooling for approximately ten minutes the CaF_2 crystal, now $\sim$ 1 mm diameter sphere was removed. The amount of Es actually incorporated in the crystal is unknown. Initially the crystal was colorless, after one hour it turned medium red, and in about 3-4 hours was dark red or black due to radiation damage.

The EPR spectrum of this crystal ($f \sim 35$ Ghz, $T = 4.2°K$) consisted of an isotropic eight line spectrum which was fitted to the parameters of a spin Hamiltonian

$$\mathcal{H} = g\beta\overline{H}\cdot\overline{S}' + A\ \overline{I}\cdot\overline{S}'$$

with $I = 7/2$ and $S' = 1/2$. Because of the large hyperfine interaction the energy expression given by the Breit-Rabi formula was used to determine the parameters; the values obtained were $|g| = 5.809 \pm 0.005$ and $|A| = (0.1216 \pm 0.002)\ cm^{-1}$. The line widths were initially about 20 gauss peak to peak (the first spectrum was obtained about 1 hour after annealing) but continually broadened due to radiation damage of the crystal, and 8 hours after annealing the spectrum was too broad to observe. The crystal could be reannealed and the spectrum regenerated.

Dipositive Es has the electronic configuration outside closed shells of $5f^{11}$ with the ground state being primarily $^4I_{15/2}$. A cubic crystalline field will split the $J = 15/2$ state into three Γ_8 quartets and two doublets, a Γ_6 and Γ_7.[6] For the likely values of the crystalline field parameters, either the Γ_6 or Γ_7 doublet should be the ground crystalline field state. The calculated g-value for the Γ_6 doublet (assuming a pure $^4I_{15/2}$ state) is -6.0 which is in reasonable agreement with the experimental value when effects of the crystalline field, spin orbit coupling, and co-valency are considered.

The crystal was radioluminescent and more reddish in appearance at 77°K than at room temperature. Spectra were recorded using a Jarrell-Ash 3/4 meter model 75-000 spectrograph. At 77°K the emission spectrum consisted of a few

relatively sharp lines superimposed upon a continuum which extended from 590 to 670 nm. At room temperature the sharp lines disappeared and the continuum extended from 560 to 700 nm. The sharpening of the broad band continuum was responsible for the color change observed at 77°K. Intense continuous absorption was observed at 77°K which started at 410 nm and probably represents a transition to a f^{10} d or charge transfer state of dipositive Es. The broad band emission could result from a transition from this state to an excited state of the f^{11} configuration. Because of the short half life of ^{253}Es the emission spectrum changed noticeably after a few half lives. Figure 1 compares the spectrum taken at two different times. Since ^{253}Es decays by α emission to ^{249}Bk ($t_{1/2}$ = 314 d) the new features which appear at 680 nm at a later time represent transitions associated with Bk ions.

The results of this investigation show that dipositive Es is more readily stabilized in CaF_2 than the earlier actinides (expecting Am). This evidence supports earlier work[1,2] which predicted that the heavier actinides should have chemically stable dipositive oxidation states.

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FOOTNOTES AND REFERENCES

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FIGURE CAPTION

Fig. 1. Radioluminescence of CaF_2:Es. Upper curve, emission spectrum 73 days after purification of Es; lower curve, spectrum 10 days after purification.

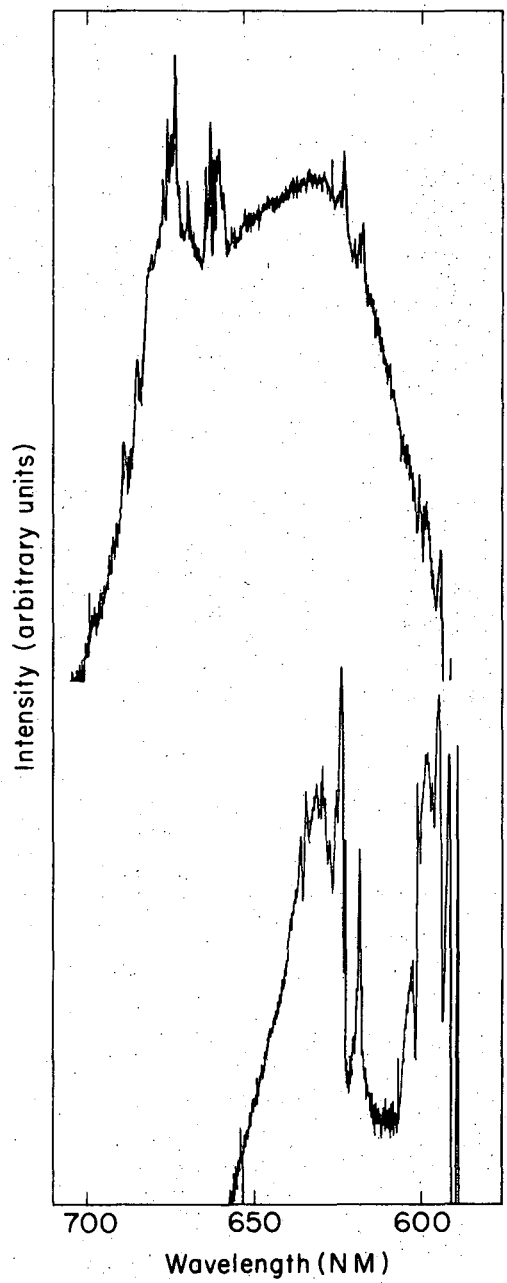

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Fig. 1.

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