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THE FORMATION AND CHARACTERIZATION OF DIVALENT AMERICIUM IN CaF_2 CRYSTALS

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In the lanthanide series of the periodic table, Eu can be readily reduced from the trivalent to the divalent state. Because of the ease of reduction of Eu^{3+} and the chemical stability of the half filled electron shell configuration, f^7, Am (the analogue of Eu in the actinide series) should be the actinide element which forms the divalent oxidation state most easily. Various attempts have been made to prepare this oxidation state of Am chemically but have met with no success.[1] Recently it has been shown that the 2+ oxidation state of all the lanthanides can be formed and stabilized in various crystal matrices. The divalent state was produced by gamma irradiation,[2] solid state electrolysis,[3] or alkaline earth metal reduction,[4] of the trivalent lanthanide in a dilute solid solution of an alkaline earth single crystal. We report herein the formation and characterization of divalent Am in single crystals of CaF_2.

Single crystals of CaF_2 each containing 0.1-0.2 weight percent of ^{243}Am (half life, 7650 years; alpha disintegrations/min-μg = 4.2×10^5; nuclear spin, I=5/2) or ^{241}Am (half life, 458 years; alpha disintegrations/min-μg = 7.2×10^6; I=5/2) were grown[5] by the Bridgman-Stockbarger technique.[6] When first removed from the furnace these crystals were light pink or tan in color, and showed considerable darkening to a brown color on standing for

periods of weeks. Electrolytic reduction[3] at approximately 600°C was performed on some of these crystals and during this process a deep reddish brown color formed first at the cathode and then spread towards the anode. There was no fluorescence in the visible region at room temperature, but heating of the radiation-damaged crystals to about 500°C caused the crystals to emit a green glow; the intensity of this glow diminished with time at constant temperature. After one hour at approximately 500°C the glow was not visible and the crystal had returned to the color it originally had after being removed from the furnace.

In single crystals of CaF_2 divalent rate earth ions substitute for the divalent Ca ions and occur in sites of cubic symmetry. The trivalent Am ion, which has an f^6 electron configuration and a $^7F_0$ electronic ground state, cannot have a paramagnetic resonance spectrum. However, divalent Am has an f^7 electron configuration and to a first approximation an $^8S_{7/2}$ ground state. In a cubic crystalline field this configuration from group theoretical considerations will split into two doublet states, Γ_6 and Γ_7, and one quartet state, Γ_8. We have found in both the radiation-reduced and the electrolytically-reduced crystals at 4°K and 1°K an isotropic paramagnetic resonance spectrum which can be fitted to the parameters of a spin Hamiltonian

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

with I=5/2 and S'=1/2. No spectrum was seen at 77°K. We find for the spectroscopic splitting factor $g = 4.490 \pm 0.002$ and for the hyperfine structure constant $A(^{243}Am) = 86.89 \pm 0.05$ gauss, $(1.821 \pm 0.002) \times 10^{-2}$ cm^{-1}; and $A(^{241}Am) = 87.64 \pm 0.05$ gauss, $(1.837 \pm 0.002) \times 10^{-2}$ cm^{-1}. The ratio of $A(^{241}Am)$ to $A(^{243}Am)$ is equal to 1.009 ± 0.001. This ratio is in excellent agreement

with the value 1.008 found in optical spectroscopy for the ratio of the hyperfine structure splittings for ^{241}Am and ^{243}Am atoms.[7] We may calculate the g values of various crystal field states using the wavefunctions for J=7/2 from the paper of Lea, Leask, and Wolf[8] and the value 1.937 for the Lande g value which is obtained from atomic beam data on ^{241}Am.[9] We find g = 4.517 for the Γ_6 state in good agreement with the experimental value. The difference between the observed and calculated g values can be attributed to the effect of covalent bonding; the mechanism for which is described by Fidone and Stevens.[10]

Optical absorption spectra of these crystals at room temperature were taken with a Cary Model 14 spectrometer and the green emission was photographed with a Jarrell Ash F/6 spectrograph. Figure 1(a) shows the spectrum of a radiation-damaged crystal about 6 weeks after preparation. The sharp lines around 5000 Å are characteristic of Am^{3+} in CaF_2. The other broad peaks we attribute to Am^{2+} for the reasons discussed below. Figure 1(b) shows the spectrum of the same crystal after heating for one hour at approximately 500°C. Only the Am^{3+} lines are present. Figure 1(c) shows the spectrum of an electrolytically-reduced crystal which was subjected to the same heat treatment as the previous crystal. As shown previously for the lanthanide series, the electrolytically-reduced species is stable to heat treatment.[3] Under some conditions we were able to obtain almost 100% conversion of the Am^{3+} to Am^{2+} as shown by the disappearance of the Am^{3+} lines in the absorption spectra. The green glow was photographed at high temperature (~500°C) and four sharp lines were resolved which were characteristic of the Am^{3+} ion. Similar results have been found for some of the rare earth ions.[11] We have also tried to electrolytically reduce the U^{3+} ion in CaF_2 by the same technique as the Am^{3+} ion. Although

the crystal darkened, the spectrum showed no new structure. If we consider this experiment as a blank for the Am experiments, then we can conclude that the radiation-reduced and electrolytically-reduced Am crystals give rise to the same new optical absorption features which are not produced in the electrolyzed CaF_2-U^{3+} crystals. Therefore we assign these new bands to Am^{2+} ions and not to color centers.

We conclude from the above results that initially Am^{3+} is present in the CaF_2 lattice but that due to the radiation from the Am decay, free electrons are formed in the lattice and some of the Am^{3+} ions are reduced to Am^{2+}. We may also do the reduction more efficiently by solid state electrolysis. Since PMR is observed only from the ground crystal field state, Γ_6, at $4^{o}K$, the crystal field splitting of the ground electronic state must be greater than 5 cm^{-1}. This splitting is much larger than the crystal field splitting of Eu^{2+} in CaF_2 (~0.1 cm^{-1}), the lanthanide analogue.

Further work is in progress on this system.

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FOOTNOTES AND REFERENCES

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Figure Captions

Fig. 1(a). Visible spectrum of a radiation-reduced Am^{2+} crystal.

(b). Visible spectrum of the above crystal after heating 1 hour at ~500°C.

(c). Visible spectrum of an electrolytically-reduced crystal after heating 1 hour at 500°C.

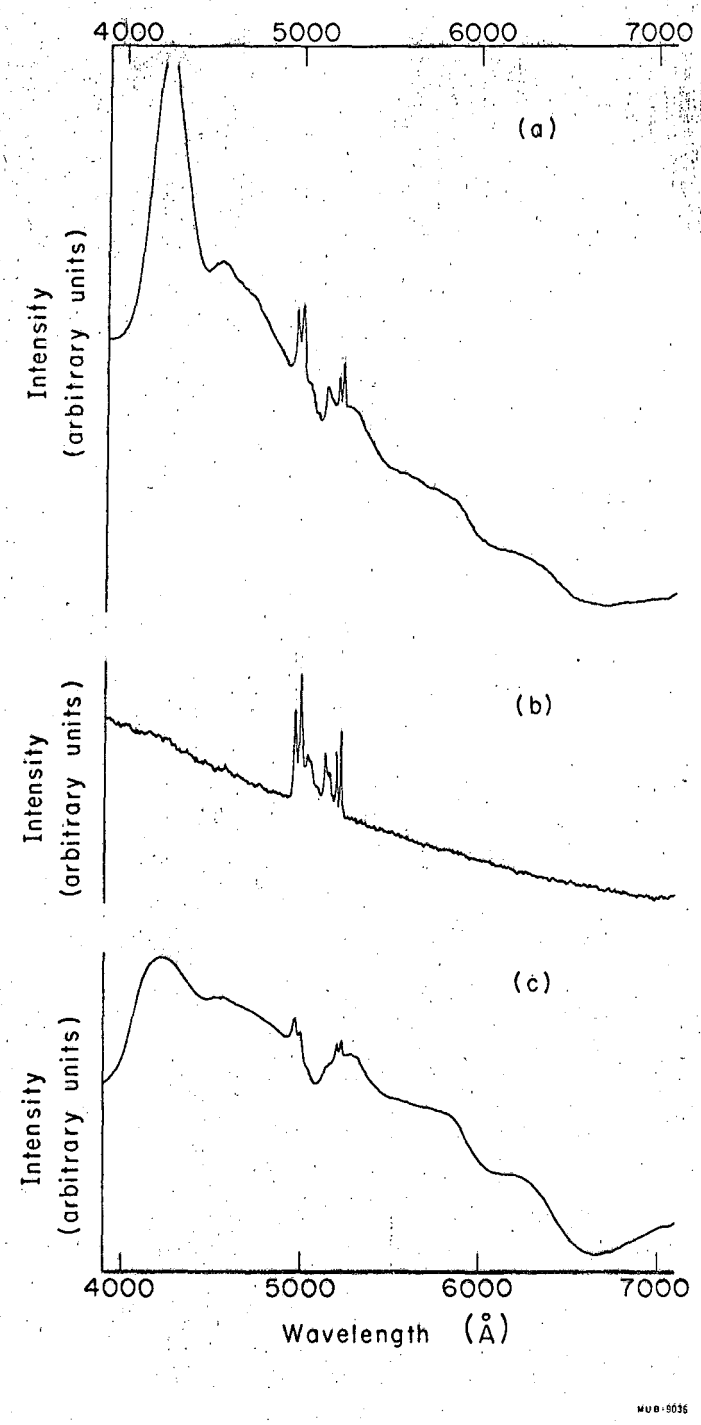
4000
5000
6000
7000
(a)
Intensity
(arbitrary units)
(b)
Intensity
(arbitrary units)
(c)
Intensity
(arbitrary units)
4000
5000
6000
7000
Wavelength (Å)
MUB-5036

Fig. 1

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