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# ELECTRON PARAMAGNETIC RESONANCE OF $Pu^{3+}$ IN CUBIC SYMMETRY SITES IN $CaF_2$, $SrF_2$ AND $BaF_2$*

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## ABSTRACT

The g values of the ground $\Gamma_7$ state of $Pu^{3+}$ in cubic symmetry sites in $CaF_2$, $SrF_2$, and $BaF_2$ are 1.297 ± .001, 1.250 ± .002, and 1.187 ± .004 respectively, as measured at $T = 1.2°K$ by EPR techniques. By fitting the g values, estimates of the crystalline field parameters are derived. It is shown that crystalline field effects for $Pu^{3+}$ in the alkaline earth fluorides are the same order of magnitude as in the lanthanide series.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

## I. INTRODUCTION

In a continuing investigation of actinide ions doped in crystals of the fluorite type,[1] we have measured the electron paramagnetic resonance (EPR) spectrum of trivalent Pu in cubic symmetry sites in $CaF_2$, $SrF_2$ and $BaF_2$. Two effects have to be taken into account in order to interpret the measured g values; the first is the effect of intermediate coupling caused by the large spin orbit coupling energies of the actinide ions on the sign and magnitude of calculated operator equivalent factors, the second is the effect of the crystalline field mixing excited J states with the ground state. In this paper we describe our experimental results and calculations from which the crystalline field parameters are approximately determined.

## II. EXPERIMENTAL

Single crystals of $^{239}Pu^{3+}$ in $CaF_2$, $SrF_2$, and $BaF_2$ were grown as described earlier.[1] The EPR measurements were made at either 1°K or 4°K with a conventional superheterodyne spectrometer operating at approximately 9.2 GHz. The magnetic field was produced by a 12-inch rotating magnet and measured either with a proton gaussmeter whose frequency was monitored by a frequency counter or by a rotating coil gaussmeter. A small amount of DPPH was placed in the cavity and was used as an internal standard. The frequency of the signal klystron was measured with a high Q wavemeter.

A trivalent ion substituted in a host such as the alkaline earth fluorides may go into a number of different site symmetries. The Pu isotope used, $^{239}Pu$ ($t_{1/2}$ = 24,360 yr), has a nuclear spin I = 1/2. In the crystals of $Pu^{3+}$ in $CaF_2$ and $SrF_2$ we found that the strongest resonance was isotropic and could be fitted to a spin Hamiltonian of the type

$$H = g\beta\, \overline{H}\cdot\overline{S}' + A\, \overline{I}\cdot\overline{S}' \qquad (1)$$

where $S' = 1/2$ and $I = 1/2$. The parameters measured are given in Table 1. Calculations of the hyperfine interaction are in progress and will be reported in a future paper. The hyperfine lines of $Pu^{3+}$ in $CaF_2$ were further split by superhyperfine structure from the cube of fluorine ions surrounding the impurity ion. This aspect of the problem is not completed. The non-isotropic resonances were much weaker and we have done no further work on them. However, we had trouble growing good $BaF_2$ crystals and in a number of these crystals we found only trigonal resonances which were fit to a spin Hamiltonian of the type

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad . \qquad (2)$$

We finally obtained a crystal which, besides the trigonal resonances, also contained a weak isotropic resonance which could be fit to the spin Hamiltonian of Eq. (1) with $S' = 1/2$ and $I = 1/2$. The results for $BaF_2$ are also given in Table 1. In all the measurements made on $Pu^{3+}$ in cubic sites we had to work at the low microwave powers ($\sim 1\ \mu w$) in order to minimize saturation effects.

## III. PRELIMINARY DISCUSSION AND RESULTS

The electronic configuration of $Pu^{3+}$ outside the closed shells is $5f^5$. The optical spectrum was originally obtained and interpreted for this ion by Lammerman and Conway[2] and refined further by Conway and Rajnak.[3] We consider the configuration $f^5$. The ground term is $^6H$ which, with the inclusion of spin orbit coupling, breaks up into a $^6H_{5/2}$ lying lowest and $^6H_{7/2}$ as the first excited state. The spin orbit interaction mixes states with different L and S but is diagonal in J so this quantum number is used to label the intermediate coupled states. For $Pu^{3+}$ in $LaCl_3$ the lowest state is $J = 5/2$ and the $J = 7/2$ first excited state is at 3190 $cm^{-1}$. The optical spectrum of $Pu^{3+}$ in $CaF_2$ shows three groups of sharp lines whose centers of gravity do not deviate more than 2.5% from those of $Pu^{3+}$ in $LaCl_3$.[2,4] Although we have not assigned this spectrum to any particular site symmetry, it is an indication that the free ion energy levels do not shift much from crystal to crystal. Therefore, we make the assumption that the free ion wavefunctions obtained by Conway and Rajnak for $Pu^{3+}$ in $LaCl_3$ are the same for the alkaline earth fluorides and accordingly use them for the calculations in this paper.

It is instructive to compare the effects of intermediate coupling on the lanthanide ion $Sm^{3+}$, $4f^5$, and on the actinide ion $Pu^{3+}$, $5f^5$. Table 2 lists the complete 28-term wavefunction for the ground $J = 5/2$ level of both ions. The wavefunction for $Sm^{3+}$ was calculated from the electrostatic and spin orbit parameters given by Carnall, Rajnak and Fields.[5] From Table 2 we see that for $Sm^{3+}$ the $^6H$ term contributes 96% to the complete wavefunction, while for $Pu^{3+}$ the $^6H$ term contributes only 66%. In any

calculation involving $Pu^{3+}$ we can not ignore the higher order terms. The importance of this fact will be seen in the crystalline field effects.

The crystalline field at cubic symmetry sites in alkaline earth fluorides is cubic, eight $F^-$ ions surround the trivalent ion. The Hamiltonian for the crystalline field is[6]

$$H_c = B_4(O_4^0 + 5\,O_4^4) + B_6(O_6^0 - 21\,O_6^4) \tag{3}$$

where $B_4$ and $B_6$ are adjustable parameters used to fit the experimental data, and the $O_n^m$ terms are angular momentum operators of the appropriate symmetry. For a pure $J = 5/2$ state the sixth-order term will be zero.

Let us now consider only the $J = 5/2$ state. In a cubic crystalline field this state will split into a doublet $\Gamma_7$ and a quartet $\Gamma_8$, with the energy level diagram as shown in Fig. 1. The cubic field splitting of the $J = 7/2$ level is also shown. The fourth degree parameter is defined as

$$\begin{aligned} b_4 &= 60\,B_4 = 60\,A_4^0 \langle r^4 \rangle \langle \psi_J \| \beta \| \psi_J \rangle \\ b_6 &= 1260\,B_6 = 1260\,A_6^0 \langle r^6 \rangle \langle \psi_J \| \gamma \| \psi_J \rangle \end{aligned} \tag{4}$$

where $\langle r^n \rangle$ is the expectation value for the f electrons, $\langle \psi_J \| \beta \| \psi_J \rangle$ and $\langle \psi_J \| \gamma \| \psi_J \rangle$ are the fourth-degree and sixth degree operator equivalent factors respectively and $A_4^0$ and $A_6^0$ may be treated as parameters or in the approximation of the point charge model, they are the fourth and sixth degree potentials at a particular point in the lattice resulting from the sum of all the charges. The definitions of Eq. (4) depend on the assumption that the

4f-wavefunction does not overlap with the electronic wavefunctions of the flourine ions. The observation of superhyperfine structure is an indication that this is not true. We can treat the angular part of the crystalline field interaction precisely by pure symmetry considerations. Later we will use the factorization $\langle r^k \rangle A_K^0$ for a crude estimate of the variation of our $B_K$ parameters in going from lanthanide ions to actinide ions. From the free ion wavefunctions we may calculate the fourth- and sixth-degree operator equivalent factors as described earlier.[1,7] Table 3 lists the second-, fourth- and sixth-degree (where applicable) operator equivalent factors for $Pu^{3+}$ and $Sm^{3+}$ for the ground $J = 5/2$ state and next highest state $J = 7/2$. The point charge model usually gives the correct sign for the splittings in the alkaline earth fluorides and for cubic symmetry $A_4^0$ is negative, $A_6^0$ is positive. From Table 3 we see that the sign of $\langle \psi_J \| \beta \| \psi_J \rangle$ is positive for $Sm^{3+}$ but negative for $Pu^{3+}$. Therefore, for $Sm^{3+}$ the $\Gamma_8$ state should be lowest but for $Pu^{3+}$ the $\Gamma_7$ is lowest as found experimentally. In the case of $Pu^{3+}$, the effects of intermediate coupling are large enough to change the sign of the fourth-degree operator equivalent factor and, thereby, reverse the crystalline field energy levels in the ground $J = 5/2$ state as compared to the $4f^5$ lanthanide $Sm^{3+}$. This is not true for the first excited state $J = 7/2$. As shown in Table 3, these operator equivalent factors have the same sign for the $f^5$ configuration in the 4f and 5f series.

If we assume that the crystalline field is small compared with the splitting between the $J = 5/2$ and $7/2$ states, we may calculate the g value of the $\Gamma_7$, $J = 5/2$ state and find it to be -.700. This does not agree with our experimental value so now we consider crystalline field

mixing of excited $J$ states. The correct way to calculate this mixture would be to simultaneously diagonalize the electrostatic, spin orbit, and crystalline field matrix elements for the $f^5$ configuration. This would require diagonalization of a very large matrix which is not feasible, so instead, we have done two calculations. In the first case we calculate matrix elements for the lowest $J = 5/2$ and $7/2$ levels using the complete free ion set of states and include crystalline field mixing between these two $J$ states. The second calculation simultaneously diagonalizes the electrostatic, spin orbit, and crystalline field matrix elements for a truncated basis set consisting of only the $^6H$ and $^6F$ terms. The second calculation gives us the wrong spin-orbit splitting between the lowest two states but allows us to estimate the error in ignoring higher $J$ states.

From group theoretical considerations, the crystalline field can mix between different $J$ levels only those states of the same symmetry. Since in the $J = 5/2$ level we are interested in the isotropic $\Gamma_7$ state, we need only consider the crystalline field mixing of the $J = 7/2$, $\Gamma_7$ state. We write the mixed wavefunction as

$$\Gamma_7^1 = \cos\phi|J = 5/2, \Gamma_7^+\rangle - \sin\phi|J = 7/2, \Gamma_7^{+'}\rangle \tag{5}$$

and so forth, where the crystalline field wavefunctions and states are given in Table 4.

Evaluation of the matrix element

$$\langle \Gamma_7^1|\vec{L}_z + 2\,\vec{S}_z|\Gamma_7^1\rangle$$

by tedious but straight-forward techniques over the complete intermediate-coupled wavefunction leads to the expression for the $g$ value of the ground crystalline field state

$$g^{1}_{1'_7} = -0.700 \cos^2 \phi + 3.254 \sin \phi \cos \phi + 2.595 \sin^2 \phi \quad . \tag{6}$$

Matrix elements of the crystalline field Hamiltonian including both the fourth-degree and sixth-degree terms were evaluated by means of the equation

$$(f^n \alpha SLJJ_z | V_c | f^n \alpha' SL'J'J'_z) = \sum_{k,q} B^k_q (f^n \alpha SLJJ_z | U^{(k)}_q | f^n \alpha' SL'J'J'_z)(f \| C^{(k)} \| f) \tag{7}$$

and by summing over the complete intermediate coupled wavefunctions.[8,9] It should be noted that the $B^k_q$ of Eq. (7), the relevant ones which we now denote as $B'_4$ and $B'_6$ are related to our earlier definition by[10]

$$\begin{aligned} B'_4 &= 8\, A^\circ_4 \langle r^4 \rangle \\ B'_6 &= 16\, A^\circ_6 \langle r^6 \rangle \quad . \end{aligned} \tag{8}$$

From summations of Eq. (7), we calculate the $2 \times 2$ energy matrix of the crystalline field Hamiltonian between the $J = 5/2$, $\Gamma^+_7$ and $J = 7/2$, $\Gamma^{+'}_7$ states:

$$\begin{pmatrix} \langle \Gamma_7^+ | V_c | \Gamma_7^+ \rangle & \langle \Gamma_7^+ | V_c | \Gamma_7^{+\prime} \rangle \\ \langle \Gamma_7^+ | V_c | \Gamma_7^{+\prime} \rangle & 3190 + \langle \Gamma_7^{+\prime} | V_c | \Gamma_7^{+\prime} \rangle \end{pmatrix} \tag{9}$$

$$= \begin{pmatrix} .01043\ B_4' & .07917\ B_4' - .23015\ B_6' \\ .07917\ B_4' - .23015\ B_6' & 3190 + .06689\ B_4' - 0.12413\ B_6' \end{pmatrix} .$$

In order to diagonalize this matrix, we have to choose values for $B_4'$ and $B_6'$. Since we have only one experimental measurement per crystal, we can fit only one parameter. Therefore, we decided to fit the $g$ values for the following approximations: 1) $B_4'$, $B_6' = 0$; 2) $B_4'$, $B_6'/B_4' = -.2$ . We consider the second approximation to be more likely because a number of lanthanide ions in $CaF_2$ have nearly this ratio.[11-14] The matrix is diagonalized for various values of $B_4'$, and the eigenvectors obtained are used in Eq. (6) to calculate $g_{\Gamma_7^1}$. Figure 2 shows plots of $g$ vs. $B_4'$ for $B_6' = 0$, and $B_6'/B_4' = -.2$ . The point charge model and experimental data on lanthanide ions show

$$|B_4'|_{CaF_2} > |B_4'|_{SrF_2} > |B_4'|_{BaF_2} .$$

Our data show that

$$|g|_{Pu^{3+}\ CaF_2} > |g|_{Pu^{3+}\ SrF_2} > |g|_{Pu^{3+}\ BaF_2} ,$$

and the arrows on Fig. 2 indicate the values for $B_4'$ which meet these conditions. Table 5 summarizes our results for $B_6'/B_4' = -.2$ .

The second type of calculation was the simultaneous diagonalization of the electrostatic spin orbit, and crystalline field matrix elements using a truncated basis set. This calculation gave the incorrect ordering of the crystalline field states in the $J = 5/2$ level and the wrong spin orbit splitting but showed that the error due to neglecting admixtures of higher $J$ states is less than 10%. Since we have approximated the value of $B_6'$, we shall assume that the effect of neglecting the mixing of these other levels is negligible. Optical work on $Ho^{2+}$ by Weaklem and Kiss[11] and on $Dy^{2+}$ by Kiss[12] in matrices of $CaF_2$, $SrF_2$ and $BaF_2$ give the values for the ratio of $B_6'$ to $B_4'$ of $-.2$ for $Ho^{2+}$ and $-.27$ for $Dy^{2+}$. Weber and Bierig[13] conclude from their survey of $Re^{3+}$ ions in cubic symmetry sites in $CaF_2$ that $-B_4' \simeq 2000 - 3400\ cm^{-1}$ and $B_6' \simeq 480 - 720\ cm^{-1}$. By extrapolation from the rare earth data, we believe that the assumption, $B_6'/B_4' = -.2$ for $Pu^{3+}$ is reasonable. From the difference in $B_4'$ values when $B_6' = 0$ and $B_6'/B_4' = -.2$ , we estimate the error in our $B_4'$ values as shown in Table 5 is ±25%. We have calculated the energy level diagram, Fig. 3, for the $J = 5/2$ and $7/2$ levels of $Pu^{3+}$ in $CaF_2$, neglecting the interactions with higher $J$ levels and assuming $B_4' = -9600\ cm^{-1}$, $B_6' = 0$; and $B_4' = -6200\ cm^{-1}$, $B_6' = 1240\ cm^{-1}$. The energies given are approximate and the calculations were done only to give a qualitative idea of the magnitude of the splittings.

## IV. DISCUSSION

It is interesting to compare the crystalline field parameters for $Pu^{3+}$, an actinide ion, with the values found for the lanthanide series. As mentioned earlier the lanthanide values in $CaF_2$ fall in the range $-B_4' \simeq +2000 - 3400\ cm^{-1}$, $B_6' \simeq 480 - 720\ cm^{-1}$, which also include the data for the divalent ions $Dy^{2+}$,[11] $Ho^{2+}$[10] and $Tm^{2+}$.[14] The number we obtain for $Pu^{3+}$ in $CaF_2$ is $-6200\ cm^{-1}$. However, $\langle r^4 \rangle$ for actinide ions will be much larger than for the corresponding lanthanides. In order to compare that part of $B_4'$ which depends only on the crystalline matrix, we divide $B_{4_{Pu^{3+}}}'$ by the ratio

$$\frac{\langle r^4 \rangle_{Pu^{3+}}}{\langle r^4 \rangle_{Sm^{3+}}}$$

on the basis of the simple model which treats $A_K^0$ and $\langle r^n \rangle$ as separable. Dr. J. Mann[15] of Los Alamos Scientific Laboratory has provided us with the values $\langle r^4 \rangle_{Pu^{3+}} = 4.811$ a.u., $\langle r^4 \rangle_{Sm^{3+}} = 1.812$ a.u. From these values we find

$$\frac{\langle r^4 \rangle_{Pu^{3+}}}{\langle r^4 \rangle_{Sm^{3+}}} = 2.65$$

and for $CaF_2$

$$\frac{-B_4'\ Pu^{3+}}{2.65} = 2340\ cm^{-1} \quad .$$

This result falls in the range of the lanthanide values. We may also compare the ratios of $B_{4_{Pu^{3+}}}'$ in $SrF_2$ and $BaF_2$ to $B_{4_{Pu^{3+}}}'$ in $CaF_2$. In

Table 6 we list these ratios along with comparable data for $Ho^{2+}$ [11] and $Dy^{2+}$ [12] and the predictions of the point charge model. We observe the decrease in the ratios of the crystalline field parameters with increasing lattice constants is similar for the two lanthanide ions and $Pu^{3+}$ but the point charge model predicts a much larger change. We have also calculated $B'_{4_{Pu^{3+}}}$ using the point charge approximation and find that the magnitude is low by about a factor of three. This result is again similar to the way this model fails for lanthanide ions. The shortcomings of this model have been discussed previously in detail.[16,17] Our results show that once the difference in $\langle r^4 \rangle$ values is taken into account, the part of $B'_4$ which depends only on the crystalline matrix is of the same magnitude for $Pu^{3+}$ in the alkaline earth fluorides as for ions in the lanthanide series.

Generalization of this conclusion to the entire actinide series is probably not justified. The chemical properties of the first members of the actinide series are not similar to those of the lanthanide series. As we move further along the actinide series, the chemical behavior becomes more "rare-earth-like". The effect of the crystalline lattice on the more extended actinide electron orbitals will decrease as Z, the atomic number, increases and the 5f shell contracts. If there are effects of the crystalline lattice in the actinide series different from the lanthanide series we would expect them to occur in alkaline earth fluorides for actinide ions with $Z < 94$.

## V. SUMMARY

From our analysis of the g values of $Pu^{3+}$ in the alkaline earth fluorides we have obtained estimates of the crystalline field parameters in the three crystals. We have shown the importance of including the complete intermediate coupled wavefunction in calculating the energy matrices. The magnitudes of the crystalline field parameters are consistent with data from the lanthanide series. The point charge model has been shown to fail in the same fashion as in the lanthanide series.

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10. In order to calculate matrix elements by the tensor operator technique it is more convenient to define the crystalline field potential differently than when using the operator equivalent method. From now on in this paper we will follow the convention used by Wybourne.[8] The crystalline field potential for cubic symmetry is

$$V_c = B_4' \left[ C_0^{(4)} + \sqrt{\frac{5}{14}} \left( C_{-4}^{(4)} + C_4^{(4)} \right) \right] + B_6' \left[ C_0^{(6)} - \sqrt{\frac{7}{2}} \left( C_{-4}^{(6)} + C_4^{(6)} \right) \right]$$

where

$$C_q^{(k)} = \left( \frac{4\pi}{2k+1} \right)^{1/2} Y_{kq}$$

and the $Y_{kq}$ are normalized spherical harmonics.

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Table 1. Spin Hamiltonian parameters for $Pu^{3+}$ in various alkaline earth fluorides obtained from EPR spectra.

| Ion | Matrix | Site | $\|g\|$ | $\|A\|$ |
|---|---|---|---|---|
| $Pu^{3+}$ | $CaF_2$ | Cubic | 1.297±.002 | 110.7±1 gauss |
| $Pu^{3+}$ | $SrF_2$ | Cubic | 1.250±.002 | 144±2 gauss |
| $Pu^{3+}$ | $BaF_2$ | Cubic | 1.187±.004 | 184±6 gauss |
| $Pu^{3+}$ | $BaF_2$ | Trigonal | $g_\perp$ = 1.300±.005 | $A_\perp$ = 372±6 gauss |
| | | | $g_\parallel$ = .80 ±.03 | $A_\parallel$ = 326±13 gauss |

Table 2. Intermediate coupled wavefunctions for $Sm^{3+}$ and $Pu^{3+}$. Percentages are listed only for those components greater than .01%.

| | $Sm^{3+}$ [a] | | $Pu^{3+}$ [b] | |
|---|---|---|---|---|
| | Coef. | Coef.$^2$ × 100 | Coef. | Coef.$^2$ × 100 |
| $^6P$ | .0002 | | .0126 | .02 |
| $^6F$ | .0114 | .01 | .1003 | 1.01 |
| $^6H$ | .9797 | 95.98 | .8121 | 65.95 |
| $^4P1$ | -.0003 | | -.0118 | .01 |
| $^4P2$ | -.0006 | | .0277 | .08 |
| $^4D1$ | .0015 | | .0338 | .11 |
| $^4D2$ | .0017 | | .0368 | .14 |
| $^4D3$ | -.0022 | | -.0437 | .19 |
| $^4F1$ | .0068 | | .0601 | .36 |
| $^4F2$ | .0003 | | .0013 | |
| $^4F3$ | -.0162 | .03 | -.1283 | 1.65 |
| $^4F4$ | -.0073 | .01 | -.0523 | .27 |
| $^4G1$ | -.1202 | 1.44 | -.3097 | 9.59 |
| $^4G2$ | .0032 | | .0727 | .53 |
| $^4G3$ | .0311 | .10 | .1106 | 1.22 |
| $^4G4$ | -.1500 | 2.25 | -.3775 | 14.25 |
| $^2D1$ | .0013 | | .0268 | .07 |
| $^2D2$ | .0023 | | .0460 | .21 |
| $^2D3$ | -.0005 | | -.0060 | |

(continued)

Table 2. Continued

| | $Sm^{3+}$ [2] | | $Pu^{3+}$ [b] | |
|---|---|---|---|---|
| | Coef. | Coef.$^2$ × 100 | Coef. | Coef.$^2$ × 100 |
| $^2D4$ | .0014 | | .0282 | .08 |
| $^2D5$ | -.0027 | | -.0538 | .29 |
| $^2F1$ | -.0089 | .01 | -.0680 | .46 |
| $^2F2$ | -.0133 | .02 | -.0986 | .97 |
| $^2F3$ | -.0013 | | -.0039 | |
| $^2F4$ | .0056 | | .0418 | .17 |
| $^2F5$ | -.0082 | .01 | -.0617 | .38 |
| $^2F6$ | -.0130 | .02 | -.1013 | 1.03 |
| $^2F7$ | -.0142 | .02 | -.0979 | .96 |

[a] Calculated from parameters given in Reference 5.

[b] Calculated from parameters given in Reference 3.

Table 3. Operator equivalent factors for $Pu^{3+}$ and $Sm^{3+}$.

| | | $\langle \psi_J \| \alpha \| \psi_J \rangle$ | $\langle \psi_J \| \beta \| \psi_J \rangle$ | $\langle \psi_J \| \gamma \| \psi_J \rangle$ |
|---|---|---|---|---|
| $Pu^{3+}$ | J = 5/2 | $4.477 \times 10^{-2}$ | $-3.476 \times 10^{-4}$ | 0 |
| | J = 7/2 | $1.820 \times 10^{-2}$ | $-4.955 \times 10^{-4}$ | $1.314 \times 10^{-4}$ |
| $Sm^{3+}$ | J = 5/2 | $4.151 \times 10^{-2}$ | $22.690 \times 10^{-4}$ | 0 |
| | J = 7/2 | $1.671 \times 10^{-2}$ | $-2.402 \times 10^{-4}$ | $1.505 \times 10^{-4}$ |

Table 4. Crystalline field states and wavefunctions for the J = 5/2 and J = 7/2 manifolds.

| | | |
|---|---|---|
| J = 5/2 | $\Gamma_7^+$ | $.4083\|5/2\rangle - .9129\|-3/2\rangle$ |
| | $\Gamma_7^-$ | $-.4083\|-5/2\rangle + .9129\|3/2\rangle$ |
| | $\Gamma_8(1)$ | $-.9129\|5/2\rangle - .4083\|-3/2\rangle$ |
| | $\Gamma_8(2)$ | $-1.000\|1/2\rangle$ |
| | $\Gamma_8(3)$ | $1.000\|-1/2\rangle$ |
| | $\Gamma_8(4)$ | $.9129\|-5/2\rangle + .4083\|3/2\rangle$ |
| J = 7/2 | $\Gamma_6^{+\prime}$ | $.6455\|7/2\rangle + .7638\|-1/2\rangle$ |
| | $\Gamma_6^{-\prime}$ | $.6455\|-7/2\rangle + .7638\|1/2\rangle$ |
| | $\Gamma_7^{+\prime}$ | $-.8660\|5/2\rangle + .5000\|-3/2\rangle$ |
| | $\Gamma_7^{-\prime}$ | $-.8660\|-5/2\rangle + .5000\|3/2\rangle$ |
| | $\Gamma_8'(1)$ | $.5000\|5/2\rangle + .8660\|-3/2\rangle$ |
| | $\Gamma_8'(2)$ | $.7638\|-7/2\rangle - .6455\|1/2\rangle$ |
| | $\Gamma_8'(3)$ | $.7638\|7/2\rangle - .6455\|-1/2\rangle$ |
| | $\Gamma_8'(4)$ | $.5000\|-5/2\rangle + .8660\|3/2\rangle$ |

Table 5. Crystalline field parameters derived from measured g values. The error in the crystalline field parameters is estimated to be ± 25%.

| Matrix | g | $B_4'$, $B_6'/B_4' = -.2$ |
|---|---|---|
| $CaF_2$ | -1.297 | -6200 $cm^{-1}$ |
| $SrF_2$ | -1.250 | -5400 $cm^{-1}$ |
| $BaF_2$ | -1.187 | -4600 $cm^{-1}$ |

Table 6. Ratio of $B_4'$ for various ions in alkaline earths fluorides to $B_4'$ for that ion in $CaF_2$. The last column gives the results predicted by the point charge model.

| | $Dy^{2+}$ [a] | $Ho^{2+}$ [b] | $Pu^{3+}$ | Point charge model |
|---|---|---|---|---|
| $CaF_2$ | 1 | 1 | 1 | 1 |
| $SrF_2$ | .89 | .85 | .87 | .745 |
| $BaF_2$ | .78 | .71 | .74 | .532 |

[a] Reference 12.

[b] Reference 11.

## FIGURE CAPTIONS

Fig. 1. Energy level diagram for the two lowest states of $Pu^{3+}$ in a cubic crystalline field. There is assumed to be no J mixing by the crystalline field.

Fig. 2. Plot of calculated g value vs. $B_4'$. The solid line describes the calculated values for $B_6' = 0$. The dotted line describes the values for $B_6'/B_4' = -.2$ . The arrows show where the experimental g values are located.

Fig. 3. Crystalline field energy levels for the parameters shown. The energies given are approximate.

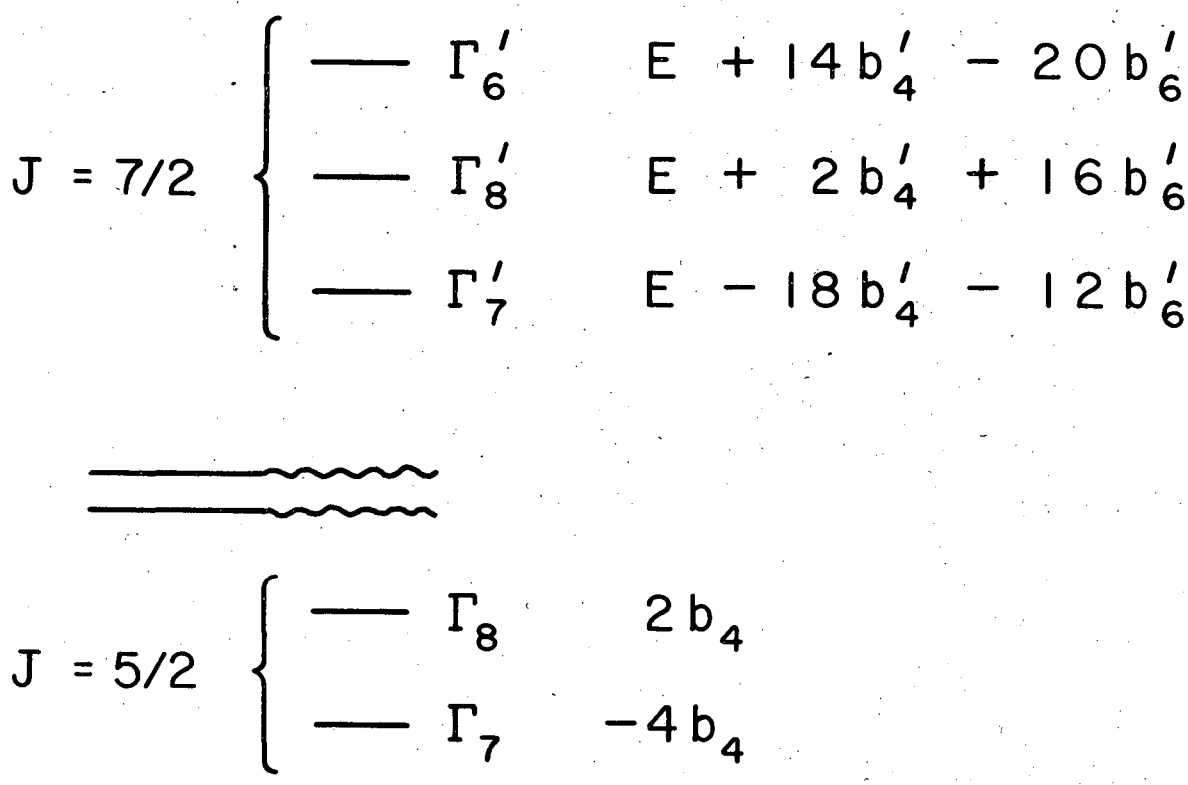


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Fig. 1.

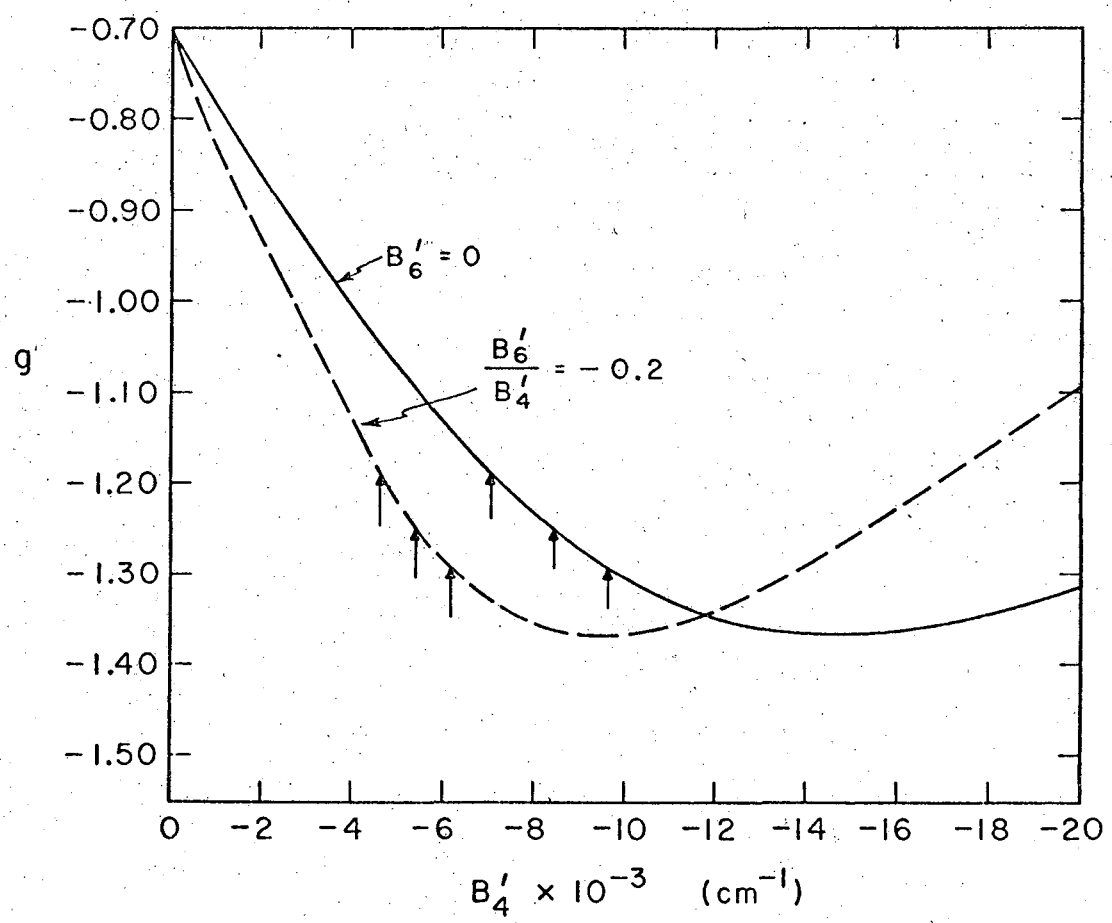


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Fig. 2.

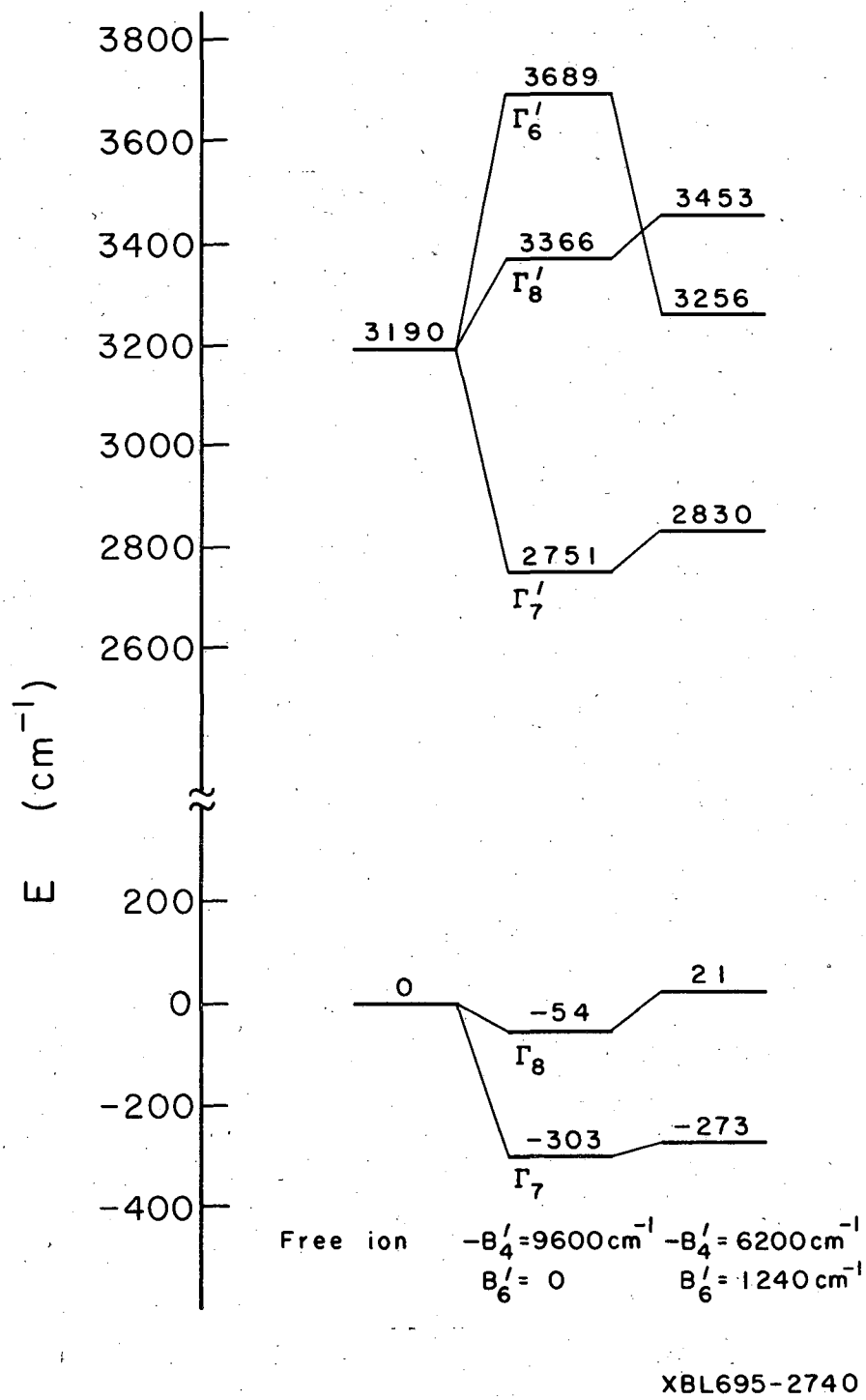


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Fig. 3.

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