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Electronic Spectra of Cesium Fluoride Complexes of Pentavalent Neptunium*

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The absorption spectra of magenta-colored $CsNpF_6$ both as a mull of the crystalline solid and as a solution in $CsF \cdot 2HF$ were obtained under various conditions. The room-temperature spectra were unique to the electronic energy levels of the seven Russell–Saunders states for the $5f^2$ configuration, split by spin–orbit coupling into 13 free-ion levels; this confirms the chemical evidence for the presence of pentavalent neptunium. At liquid-nitrogen temperatures the spectra of $CsNpF_6$ mulls were interpreted in terms of the free-ion f–f transitions of Np^{5+} split by an O_h crystal field. Term assignments to the following experimental energy levels obtained at room temperature were made on the basis of the observed Stark splitting in the low-temperature spectra, and agreement with calculated energy levels (in cm^{-1}): $^3F_2 = 4337$, $^3H_5 = 8425$, $^3F_3 = 8797$, $^3F_4 = 9701$, $^3H_6 = 13\,738$, $^3P_0 = 16\,129$, $^1D_2 = 16\,736$, $^1G_4 = 18\,265$, $^3P_1 = 19\,531$, $^1I_6 = 20\,619$, $^3P_2 = 26\,667$. All levels above the $^3H_4$ ground state were observed except $^1S_0$. A least-squares fit of these experimental energy levels was made to the Racah Coulomb interaction parameters, $E^1 = 2807$ cm^{-1}, $E^2 = 19.98$ cm^{-1}, $E^3 = 284.1$ cm^{-1}; the spin–orbit coupling parameter $\zeta = 2316$ cm^{-1}; and the configuration-interaction parameters, $\alpha = 2.7$ cm^{-1} and $\beta = 52.9$ cm^{-1}. The position of the $5f^2$ levels of Np^{5+} on the intermediate coupling diagram compared to the f^2 levels of the isoelectronic series Pr^{3+}, Nd^{4+}, Th^{2+}, U^{4+}, and Pu^{6+} (in PuF_6) was intermediate between U^{4+} and Pu^{6+} as expected.

INTRODUCTION

In recent years, the characteristic spectra of actinide element f–f transitions have been under intensive theoretical and experimental investigation. These studies yield information concerning the oxidation state, coordination number, and ligand field environment along with actual identification of the specific actinide. Observation and interpretation of spectra of common oxidation states of the actinides[1–8] have been extended to include less stable configurations of actinides through curium,[9–11] and of berkelium,[12] californium,[13] and einsteinium.[14] Reisfeld and Crosby[15] correlated their spectra of $5f^1$ pentavalent uranium in $CsUF_6$ with the isoelectronic species Cs_2PaCl_6 and NpF_6 in terms of an octahedral structure (the distortion is slight). Judd[16] found good agreement on comparing the free-ion levels of the f^2 configuration in $4f^2$ Pr^{3+}, $5f^2$ Th^{2+}, and $5f^2$ U^{4+}. Steindler and Gunther[17] have examined the spectrum of $5f^2$ Pu^{6+}.

The present work describes spectral studies of $CsNpF_6$ in both solid and solution phases. These studies were initiated partially to confirm the pentavalent state of neptunium in this compound, to provide confirmatory information regarding the symmetry of the fluoride coordination polyhedron in the complex, and to examine the $5f^2$ configuration in the hitherto undescribed M^{5+} case.

EXPERIMENTAL

Preparation of Samples

Np^{4+}

Weighed samples of green $^{237}NpO_2$ were dissolved in HCl containing a trace of HF. The neptunium was precipitated with excess HF and the resulting NpF_4 was evaporated to dryness.

Np^{5+}

The detailed preparation of Np^{5+} in solid $CsNpF_6$ [18a] and in solution in molten $CsF \cdot 2HF$ (mp $= 50°C$) has been described elsewhere.[18b]

Technique

Samples of freshly prepared NpF_4 or $CsNpF_6$ were mulled with fluorocarbon oil (Hooker Chemical Company) and mounted between sapphire flats for spectral examination at room temperature and at LN_2 (liquid-nitrogen temperature). A Cary Model CD 151-A cold cell and a Cary Model 14-MR spectrophotometer were used for these studies.

Kel-F tubes fitted to a manifold with Teflon-seated monel valves (Autoclave, Incorporated) were used for the melt studies. Anhydrous HF gas was condensed on suitable amounts of CsF and NpF_4 in these tubes to give approximately $0.01M$ solutions of Np^{4+} in $CsF \cdot 2HF$ at $100°C$. Fluorine was then admitted to destroy traces of water and to prepare $CsNpF_6$; the oxidation of $Np(IV)$–$Np(V)$ could be followed by color changes. These tubes were disconnected from the manifold and mounted directly in the spectrophotometer sample compartment.

RESULTS

Spectra

Np^{4+}

The room-temperature spectrum of NpF_4 dissolved in $CsF \cdot 2HF$ (shown in Fig. 1) is typical of a "many-

electron" system. No maxima of the $5f^3$ Np^{4+} spectrum could be investigated at wavelengths less than 4000 Å or greater than 14 000 Å due to the strong absorption of CsF·2HF and the scattering effect of Kel-F. The spectrum of NpF_4 in a fluorocarbon mull at LN_2 gave a more complicated splitting pattern indicating low symmetry for the crystal field. No attempt was made to interpret the Np^{4+} spectra but the data were useful since tetravalent neptunium is a logical impurity in the preparation of Np^{5+}.

Np^{5+}

The room-temperature spectrum of $CsNpF_6$ dissolved in CsF·2HF is also shown in Fig. 1. The spectrum was much simpler than that of NpF_4 in the same medium and analysis of the observed maxima appeared feasible.

The room-temperature spectrum of $CsNpF_6$ in a fluorocarbon mull is shown in Fig. 2. The similarity of these spectra in the melt (Fig. 1) and in the mull (Fig. 2) at wavelengths less than 13 000 Å is obvious. In Table I the observed levels of a second preparation of a fluorocarbon mull of $CsNpF_6$ are compared at ambient temperatures and at LN_2 including comments on line intensities and splitting patterns. Considerable sharpening, accompanied by increased intensity and resolution, resulted from the studies at the lower temperature.

Level Assignments

Predictions derived from the intermediate coupling diagram for the f^2 isoelectronic species[16],[19] indicate
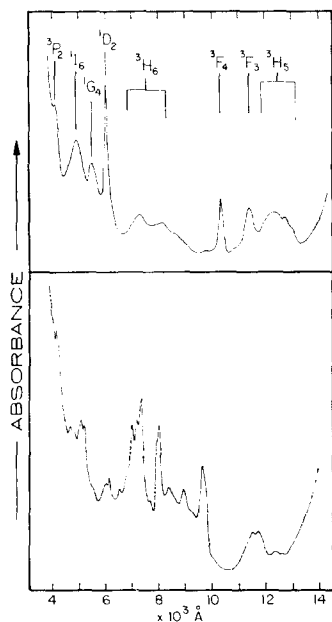

FIG. 1. Absorption spectra from 3000–14 000 Å of Np(IV) (bottom) and Np(V) (top) in CsF·2HF at room temperature.
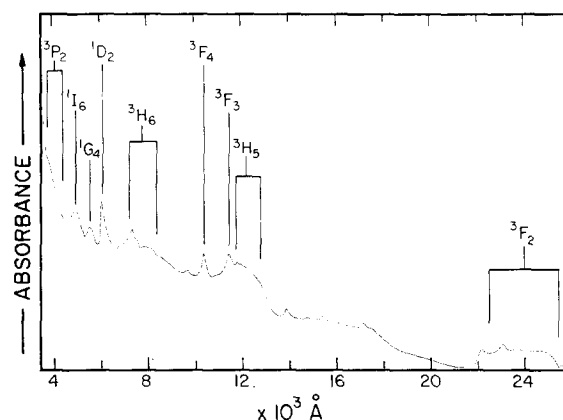

FIG. 2. Absorption spectrum from 3500–26 000 Å of a fluorocarbon mull of solid $CsNpF_6$ at room temperature. It is interesting to note that the strong transitions shown here for this weak-field fluoride complex appear to obey the free-ion magnetic-dipole selection rule, $\Delta J = 0$, ± 1; or the electric-quadrupole selection rule, $\Delta J = 0$, ± 1, ± 2. The weak $^3P_0$ and $^3P_1$ maxima are not apparent here but were discernible in the original spectrum (see Table III).

considerable mixing of the Np^{5+} levels due to the large spin–orbit interaction alone. Perturbations of the electronic energy levels due to environmental effects should also be considerable in the case of the actinides compared to the lanthanides due to the lesser shielding of the $5f$ orbitals. It was assumed (and later borne out by the results) that the principal environmental effect was Stark splitting of the free-ion levels in the crystal field.

Single-crystal data were not available for $CsNpF_6$ although x-ray powder diffraction data[18a] indicate rhombohedral symmetry isostructural with $CsUF_6$.[20a] The UF_6^- ion in $CsUF_6$ has been found to exhibit slight trigonal distortion[20a],[20b] of the octahedral configuration. Spectral studies on polycrystalline UF_6 and PuF_6[21] indicate tetragonal distortion of the hexafluoride octahedra in the low-temperature orthorhombic phase.

Wybourne (Ref. 5, page 179) lists the maximum splitting as a function of the quantum number J for all symmetries and those data were used to correlate our assignments to the related $S'LJ$ terms for NpF_6^- in Table I. Also indicated in Table I are the number of levels observed for each spectral grouping at LN_2 and at room temperature. With the exception of $^1D_2$ in which too few levels were observed and $^3P_2$ in which too many levels were observed, the theoretical maximum number of levels for a particular J value agreed exactly with the crystal-field splitting expected of the cubic symmetry class. The excess number of levels in the region of $^3P_2$ could be attributed to Np(IV). As a first approximation, we will consider the NpF_6^- species to be octahedral with O_h point-group symmetry.

Interpretation of the simple splitting patterns shown in Table I was based on evidence for the dominant population of a single ground-state level from which the

TABLE I. A comparison of crystal-field splitting in the room-temperature and cold spectra of $CsNpF_6$ mulls (second preparation).[a]

Term assignment	Observed maxima (Å)		No. of observed levels at LN$_2$	Theoret. maximum splitting			
	RT	LN$_2$		Cubic	Hexag.	Tetrag.	$2J+1$
$^1S_0$	...	...	...				
				1	1	1	1
$^3P_0$	...	6 200 sh	1				
$^3P_1$	...	5 170	1	1	2	2	3
$^3F_2$	...	25 700	2				
		24 500					
$^1D_2$	5 990	5 985 vs	1				
$^3P_2$	4 100	4 100		2	3	4	5
	3 700	3 910					
		3 790 s	5				
		3 740 vs					
		3 670 sh					
$^3F_3$	11 380	11 880	3	3	5	5	7
		11 700					
		11 450 vs					
$^3H_4$	Ground state		...				
$^3F_4$	10 300	10 860 w					
		10 625					
		10 295 vs	4				
		9 660 w		4	6	7	9
$^1G_4$	5 450	5 800 vw					
		5 625 s					
		5 480 s	4				
		5 300 vw					
$^3H_5$	12 700	13 000 sh					
	12 220	12 810 s					
	11 750	12 500 vs	4	4	7	8	11
		12 125 w					
$^3H_6$	8 500	8 685					
	8 000	8 115 s					
	7 280	7 850 sh					
		7 520 w	6				
		7 290					
		7 065					
				6	9	10	13
$^1I_6$	4 800	5 170					
		5 025 s					
		4 950 s	6				
		4 820 s					
		4 625					
		4 560					

[a] sh, shoulder; vw, very weak; w, weak; s, strong; vs, very strong (all peaks were sharp).

spectra originate. This conclusion was based on Brown's calculations[22] of the combined Coulomb, spin–orbit, and crystal-field matrix elements for f^2 in O_h; these were used to estimate the crystal-field split levels of the $^3H_4$ ground state of Np^{5+} in an O_h field. The calculated levels are shown in Table II.

From the Boltzmann equation, $E=kT$ ($k=0.695$ cm^{-1}/deg), the most probable energy for the ground state is 54 cm^{-1} at 77°K giving the value 0.001 for the relative population of the first level above the ground state (367 cm^{-1}). Even at 298°K, the relative population of the first level is less than 0.19. Therefore, it was

TABLE II. Energies of the $^3H_4$ level of Np^{5+} in an O_h field.[a]

$^3T_2$	1058 cm^{-1}
^3E	580 cm^{-1}
$^3T_1$	367 cm^{-1}
$^3A_1$	Ground

[a] A reasonable value of 0.14 was used for the relative strength of the fluoride ligand field. A complete crystal-field intermediate coupling diagram for f^2 in O_h is currently being calculated.

concluded that the number of peaks observed in a discrete spectral grouping at LN_2 was a valid measure of the number of levels in a specific state.

CALCULATIONS

Least-Squares Parameter Fits

The greater overlap of the $5f$, $6s$, $6p$, $6d$, and $7s$ actinide radial wavefunctions relative to the corresponding $4f$, $5s$, $5p$, $5d$, and $6s$ functions of the lanthanides influences the spectra of the actinides in several ways. First, the greater overlap of the $5f$ orbitals with outer orbitals increases the influence of crystal-field environmental effects when considering f–f transitions within the actinides. Second, interaction between configurations having the same parity becomes more probable as overlap increases. This configuration interaction, although weak for trivalent lanthanides,[23] becomes quite important in the interpretation of spectra of actinides such as Pu^{3+},[24] Cm^{3+},[2b] and Cf^{3+}.[13]

An iterative least-squares program was used to treat the room-temperature spectrum of Fig. 2, including the forbidden transitions $^3P_0$ and $^3P_1$. This program fits the energy levels to six adjustable parameters; E^1, E^2, and

TABLE III. Observed and calculated free-ion electronic energy levels of Np^{5+} in $CsNpF_6$ (Fig. 2).[a]

Term assignment	Observed (RT)	Calculated	Percent composition
$^1S_0$	...	39 065	87
$^3P_2$	26 667	26 481	51
$^1I_6$	20 619	21 686	86
$^3P_1$	19 531	19 547	100
$^1G_4$	18 265	17 827	35
$^1D_2$	16 736	17 305	41
$^3P_0$	16 129	15 276	87
$^3H_6$	13 738	13 497	86
$^3F_4$	9 701	9 354	36
$^3F_3$	8 797	9 881	100
$^3H_5$	8 425	7 690	100
$^3F_2$	4 337	4 132	85
$^3H_4$	...	0.0	82

[a] rms deviation is 851 cm^{-1}. (Note the rms deviation is 863 cm^{-1} for the room-temperature spectrum of Table I.)

TABLE IV. Coulomb, spin–orbit, and configuration-interaction parameters used to calculate the free-ion levels given in Table III.

Racah Coulomb interaction parameters:	$E^1 = 2807$ cm^{-1}
	$E^2 = 19.98$ cm^{-1}
	$E^3 = 284.1$ cm^{-1}
Spin–orbit coupling parameter:	$\zeta = 2316$ cm^{-1}
Configuration-interaction parameters:	$\alpha = 2.7$ cm^{-1}
	$\beta = 52.9$ cm^{-1}

E^3, the Racah Coulomb interaction terms[25]; ζ, the spin–orbit coupling parameter; and α and β, the configuration-interaction parameters.[23] The program, originating at LRL, Berkeley, uses the combined Coulomb and spin–orbit matrix elements of Nielson and Koster.[26] Configuration-interaction matrix elements were added at LRL, and the program incorporates useful modifications by Clark[27] and Ryan.[28] The calculated energy levels and the rms deviation are given in Table III. The best parameter set is given in Table IV. These results indicate a "harder" $5f$ radial eigenfunction and less overlap in the radial electron density for Np^{5+} than for a typical actinide of lower oxidation number.
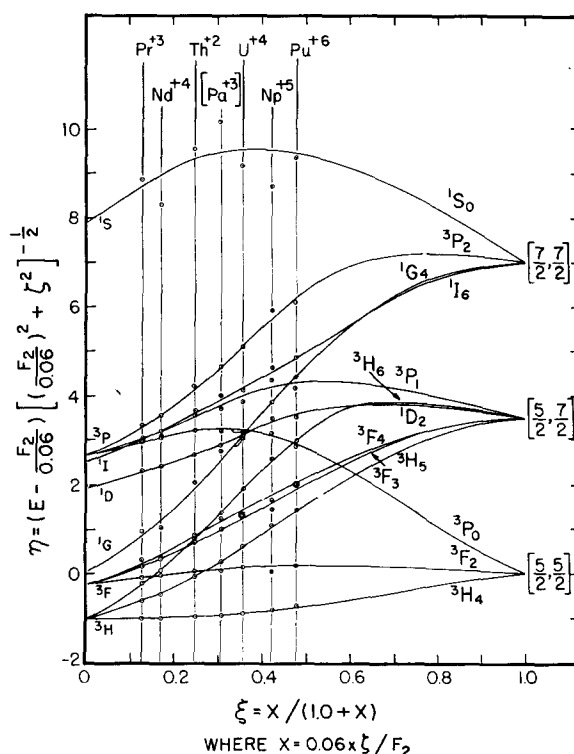

FIG. 3. The levels of the f^2 configuration in intermediate coupling. Points at $\xi = 0$ for the hypothetical pure Russell–Saunders case were calculated using $F_2 = 500$ and $\zeta = 1 \times 10^{-6}$; points at $\xi = 1$ for pure jj coupling were calculated using $F_2 = 1 \times 10^{-6}$ and $\zeta = 1 \times 10^4$.

TABLE V. Parameters used to calculate the free-ion levels of Fig. 3.

Ion	Configuration	cm^{-1}				Reference
		F_2	F_4	F_6	ζ	
Pr^{3+}	$4f^2$	305.4	51.88	5.321	730	6
Nd^{4+}	$4f^2$	357	51.6	5.28	1142	19
Th^{2+}	$5f^2$	193	36.3	3.4	1035	16
(Pa^{3+})[a]	$5f^2$	200	$\cdots$	$\cdots$	1458	This work
U^{4+}	$5f^2$	206	$\cdots$	$\cdots$	1870	16
Np^{5+}	$5f^2$	212	43.2	5.37	2341	29 and this work
Pu^{6+}	$5f^2$	217	$\cdots$	$\cdots$	3270	17 and this work

[a] Estimated.

The Levels of the f^2 Configuration in Intermediate Coupling

Correlation between the $S'LJ$ states of $4f^2$ Nd^{4+} determined previously[19] and some typical results with $5f^2$ Np^{5+} was made to the intermediate coupling diagram of Judd's (Ref. 16, Fig. 4-1). This was accomplished by recalculating Judd's diagram for all ions of the f^2 configuration in terms of modified ordinate and abscissa values using the Slater Coulomb-interaction parameter F_2 as described in Ref. 19 and shown in Fig. 3.

The levels of Pr^{3+} in this figure were calculated from the parameters listed by Wybourne[6] while levels of the postulated Pa^{3+} were calculated by linear interpolation of F_2 and ζ between Th^{2+} and U^{4+} assuming the $5f$ radial eigenfunctions to be hydrogenic. The levels of Np^{5+} were obtained from parameter fits to spectral data described earlier.[29] The Pu^{6+} levels plotted in Fig. 3 were calculated from the spectral data of Steindler and Gunther[17] on gaseous plutonium hexafluoride. All parameters are listed in Table V.

Comparison of the Spectra of PuF$_6$ and NpF$_6^-$

The absorption spectra of gaseous PuF$_6$ shown in Fig. 4 include the level assignments made here to the data of Steindler and Gunther.[17] The similarities between the spectra of isoelectronic PuF$_6$ and NpF$_6^-$ are apparent (see Figs. 2 and 4). The best-defined levels of PuF$_6$, $^3F_2$, $^3H_5$, and the $^3F_{3-4}$ pair (the four lower energy terms), were found to have corresponding maxima in NpF$_6^-$. Inspection of the $^3H_5$ term for PuF$_6$ indicates seven levels which is the number of crystal-field split levels predicted in Table I for structures of hexagonal symmetry at $J=5$. This value is consistent with the number of levels expected of a hexafluoride octahedra under tetragonal distortion. The neptunium spectra were examined for vibronic coupling interac-

tions similar to the analysis of the PuF$_6$ spectra,[17] but no obvious correlations were found.

CONCLUSIONS

The spectral evidence for the $5f^2$ configuration of pentavalent neptunium in CsNpF$_6$ is quite conclusive. The calculated parameters follow the trend expected from previous work on isoelectronic species and clearly
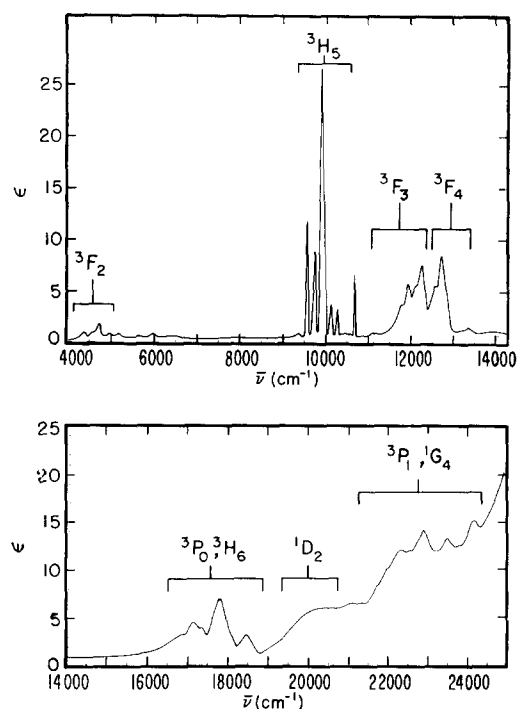

FIG. 4. Absorption spectra and term assignments of gaseous plutonium hexafluoride. ϵ is in units of liters/mole·cm^{-1}. The spectra are from Steindler and Gunther.[17]

confirm the general features of our assignments. The discrepancy between the calculated and observed levels may arise from causes such as: difficulty in assigning the band centers due to the intrinsic breadth of the peaks as well as vibronic coupling; improper assignment of levels arising from impurities having appreciable oscillator strengths; a point-group symmetry for NpF_6^- other than O_h; and shifts in levels when higher-order corrections in the theory are considered.

Ideally studies of single crystals of $CsNpF_6$ at liquid-helium temperatures should obviate these difficulties. However, even at present, considering the limitations imposed, the use of spectral data to obtain an estimate of the symmetry of the crystal field appears promising. Indeed, pure single crystals of some of the highly radioactive actinide compounds may never become available, in which case techniques involving spectra of microcrystalline powders (mulls) and of solutions, will prove of great value.

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[1] J. G. Conway and R. D. McLaughlin, J. Opt. Soc. Am. 46, 91 (1956).

[2] (a) J. B. Gruber, J. Inorg. Nucl. Chem. 25, 1093 (1963); (b) J. B. Gruber, W. R. Cochran, J. G. Conway, and A. T. Nicol, J. Chem. Phys. 45, 1423 (1966).

[3] J. L. Ryan, Inorg. Chem. 2, 348 (1963).

[4] W. T. Carnall and B. G. Wybourne, J. Chem. Phys. 40, 3428 (1964).

[5] B. G. Wybourne, Spectroscopic Properties of Rare Earths (Interscience Publishers, Inc., New York, 1965).

[6] B. G. Wybourne, J. Opt. Soc. Am. 55, 928 (1965).

[7] L. B. Asprey and T. K. Keenan, J. Inorg. Nucl. Chem. 7, 27 (1958); see also W. T. Carnall, P. R. Fields, D. C. Stewart, and T. K. Keenan, ibid. 6, 213 (1958).

[8] R. A. Penneman and T. K. Keenan, "The Radiochemistry of Americium and Curium," NAS-NS 3006, USAEC, January 1960.

[9] L. B. Asprey, F. H. Kruse, and R. A. Penneman, Inorg. Chem. 6, 544 (1967).

[10] L. B. Asprey and R. A. Penneman, Inorg. Chem. 1, 134 (1962).

[11] T. K. Keenan, J. Am. Chem. Soc. 83, 3719 (1961).

[12] R. G. Gutmacher et al. UCRL-70202, November 1966; see also R. G. Gutmacher, et al., J. Inorg. Nucl. Chem. 29, 2341 (1967).

[13] J. L. Green, Inorg. Nucl. Chem. Letters 2, 365 (1966).

[14] R. G. Gutmacher, E. F. Worden, and J. G. Conway, 155th National ACS Meeting, San Francisco, Calif., 1968, Div. Nucl. Chem. Tech., Paper #33.

[15] M. J. Reisfeld and G. A. Crosby, Inorg. Chem. 4, 65 (1965).

[16] B. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill Book Co., New York, 1963).

[17] M. J. Steindler and W. H. Gunther, Spectrochim. Acta 20, 1319 (1964).

[18] (a) L. B. Asprey, T. K. Keenan, R. A. Penneman, and G. D. Sturgeon, Inorg. Nucl. Chem. Letters 2, 19 (1966). (b) R. A. Penneman, T. K. Keenan, and L. B. Asprey, Advan. Chem. Ser. 71, 248 (1967).

[19] L. P. Varga and L. B. Asprey, J. Chem Phys. 49, 4674 (1968).

[20] (a) A. Rosenzweig and D. T. Cromer, Acta Cryst. 23, 865 (1967). (b) P. Rigny and P. Plurien, J. Phys. Chem. Solids 28, 2589 (1967).

[21] R. Blinc, E. Pirkmajer, J. Slivnik, and I. Zupancic, J. Chem. Phys. 45, 1488 (1966).

[22] J. D. Brown, University of Canterbury, Christchurch, New Zealand (private communication, 1968).

[23] K. Rajnak and B. G. Wybourne, Phys. Rev. 132, 280 (1963).

[24] J. G. Conway and K. Rajnak, J. Chem. Phys. 44, 348 (1966).

[25] G. Racah, Phys. Rev. 76, 1352 (1949).

[26] C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations (Technology Press, Cambridge, Mass., 1963).

[27] F. L. Clark, Argonne National Lab. (private communication, 1967).

[28] R. R. Ryan, Los Alamos Scientific Lab. (private communication, 1967).

[29] L. P. Varga, L. B. Asprey, R. A. Penneman, and T. K. Keenan, 155th National ACS Meeting, San Francisco, Calif., 1968, Div. Nucl. Chem. Tech., Paper #34.