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**Comparison of the Electronic Structure of the
Lanthanides and Actinides**

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Abstract

This paper reviews the electronic structure of the 4f and 5f compounds. To this end the optical and magnetic analyses of similar compounds are compared. In most cases this entails comparing trivalent actinide with trivalent lanthanide compounds although the f^1 configuration (Ce^{3+} diluted in Cs_2NaYCl_6 and Pa^{4+} diluted in Cs_2ZrCl_6) will be treated in detail. In general the ground electronic states for lanthanide and actinide compounds with the same number (n) of f electrons (f^n) and the same coordination about the metal ions are similar, although the total crystal field splitting in the actinides is approximately twice as great as for the lanthanides. The half-filled shell, f^7 , is a special case with a relatively large ground state splitting in the $5f^7$ ground term caused by the effects of the much larger spin-orbit coupling.

Introduction

The lanthanide series consists of the fourteen elements following lanthanum in the periodic table and is formed by the successive addition of a 4f electron to the electronic configuration of lanthanum. Because the 4f shell is an inner shell, the chemistry of the lanthanide ions are in general very similar. Although the chemical properties of the early actinide ions are quite different

Key words: electronic structure, actinides, lanthanides, crystal field, optical spectra

from those of the later actinide ions and the lanthanide series, the actinide series, in analogy with the lanthanide series, is defined as the fourteen elements following actinium in the periodic table.

The 4f orbitals in the lanthanide series are inner orbitals and do not participate in chemical bonding. In the early actinides the 5f orbitals are more extended and very close in energy to the 6d orbitals. As the atomic number increases, the 5f orbitals become more localized and progressively lower in energy relative to the 6d configuration. The relative energies of the d orbitals (5d for the lanthanides and 6d for the actinides) relative to the f configuration for the trivalent ions are shown in Figure 1. The data are taken from Brewer[1]. It is instructive to plot the mean radius $\langle r \rangle$ of the lanthanide and actinide ions as a function of atomic number (Figure 2). Here the mean radius is defined as follows:

$$\langle r^k \rangle = \int_0^\infty P_{nl}^*(r) r^k P_{nl}(r) dr$$

where $P_{nl}(r)$ is the radial wavefunction with principal quantum number n , angular momentum quantum number l , and $k=1$. All quantities are in atomic units.

Ionic radii for the lanthanide and actinide ions [3] are also plotted in Figure 2. Note the mean radii are consistently larger for the actinide series than for the lanthanides although the ionic radii for the two series are much closer to one another. This is because the ionic radii are determined not only by the f wavefunctions but also by the closed 5s²,5p⁶ (6s²,6p⁶) shells. Plots of the relevant wavefunctions for Nd³⁺ and U³⁺ are shown in Figure 3.

For the first half of the actinide series, a large number of compounds are known with formal oxidation states ranging from 2+ to 7+. Molecular compounds of actinide ions in higher oxidation states are well known. Some

examples include the AnF_6 ($An = U, Np, \text{ and } Pu$), the transuranium borohydrides, $An(BH_4)_4$, ($An = Np, Pu$), and dimeric compounds such as $[U(OC_2H_5)_5]_2$. The lighter members of the borohydride series are polymeric (Th, Pa, and U), but the Np and Pu compounds are monomeric and their physical properties resemble monomeric $Zr(BH_4)_4$ much more than polymeric $U(BH_4)_4$. Organometallic compounds are known for both the lanthanide and actinide series. If the ligand is large enough so as to prevent further coordination of other ligands by its steric bulk, then monomeric molecular compounds can be formed in both series. The early tetravalent actinides form organometallic compounds rather readily, and a number of these compounds show remarkable stability. For compounds of the type $[C_8H_8]_2An$, ($An = Th, Pa, U, Np, Pu$) the stability of uranocene, $U[C_8H_8]_2$ has been attributed to covalent bonding between the e_{2u} orbitals of the cyclooctatetrane rings and the e_{2u} f orbital [5]. Variable energy photoelectron studies [6] as well as ab initio calculations [7] show that the 6d e_{2g} orbitals and the e_{2g} orbitals of the rings make a substantial contribution to the bonding.

The purpose of this paper is to compare the electronic structures of the 4f and 5f compounds. To this end the optical and magnetic analyses of similar compounds will be compared. In most cases this will entail comparing trivalent actinide with trivalent lanthanide compounds except for the f^1 configuration. First of all the standard parametric theory used in the analysis of optical and magnetic data for f^n ions will be reviewed.

Parametric Theory [8,9]

The energy levels of an f^n ion are obtained by simultaneous diagonalization of the free-ion (H_{FI}) and crystal-field (H_{CF}) Hamiltonians:

$$\begin{aligned}
H_{FI} = & \sum_{k=0,2,4,6} F^k(nf,nf) f_k + \zeta_f \alpha_{s.o.} + \alpha L(L+1) \\
& + \beta G(G_2) + \gamma(R_7) + \sum_{\substack{k=2,8 \\ k \neq 5}} T^k t_k \\
& + \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k
\end{aligned}$$

and

$$H_{CF} = \sum_{k,q} B_q^k C_q^k$$

The $F^k(nf,nf)$ and ζ_f parameters above represent the radial part of the electrostatic interaction between two f electrons, and the spin-orbit interaction, respectively, while f_k and $\alpha_{s.o.}$ are angular parts of these interactions. The parameters α, β, γ are associated with the two-body effective operators of the configuration interaction, and the T^k s are the corresponding parameters of the three-body configuration interaction operators. The M^k parameters represent the spin-spin and spin-orbit interactions, and the P^k parameters arise from electrostatic-spin-orbit interactions with higher configurations. The number of B_q^k parameters in the crystal-field Hamiltonian is determined by the site symmetry of the metal ion. The angular operators C_q^k are the usual Racah parameters and can be evaluated by standard techniques [10].

The parameters that have a major effect on the calculated spectra are the Slater parameters $F^k(nf,nf)$, the spin-orbit coupling constant ζ_f , and the crystal-field parameters. Assignments of the observed energy levels are made and then compared with those calculated with assumed parameters from the above

Hamiltonian. New assignments are then made and the parameters adjusted by a least squares routine to obtain the best fit between experiment and calculation. The "best" fit is obtained when the value of σ (in cm^{-1}) is at a minimum where

$$\sigma = [\sum (E_{\text{obs.}} - E_{\text{calc.}})^2 / (n - p)]^{1/2}$$

where $E_{\text{obs.}}$, $E_{\text{calc.}}$ are the observed and calculated energies, n the number of observed levels, and p the number of parameters varied.

The wavefunctions and energy splittings determined from the above Hamiltonian can be used to calculate magnetic susceptibility as a function of temperature, magnetic dipole transition strengths, and g values for crystal-field states. Some representative values for the parameters of the Hamiltonian for some trivalent lanthanide and actinide ions in LaCl_3 are given in Table 1.

For the f^1 case the Hamiltonian is considerably simplified as the only parameters in this case are the spin-orbit coupling constant and the crystal-field parameters. For the f^2 case all three-body operators are zero.

The f^1 ion in octahedral symmetry

The two systems, $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ and $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$, have been thoroughly studied [11-14]. In both cases the $4f^1$ or $5f^1$ ion is surrounded by 6 Cl^- ions in an octahedral array. Both systems show fluorescence from the lowest level of the excited d configuration (at $\sim 28,000 \text{ cm}^{-1}$ for Ce^{3+} and $20,000 \text{ cm}^{-1}$ for Pa^{4+}) to the f configuration, and the energies of four of the five expected crystal field states of the f configuration are accurately determined. These energies may

be fit by diagonalizing the matrices obtained from an empirical Hamiltonian and adjusting the parameters to this Hamiltonian. In this simple case there are two crystal-field parameters and one spin-orbit coupling parameter. Since there are three energy differences and three parameters, the fit is perfect. However the fit may be checked by calculating the ground state g values and comparing them to the experimental values. The results are shown in Table 2.

Note that for $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ the agreement is excellent, but for $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ the calculated g value is quite a bit off from the experimental value. This is a general result when actinide and lanthanide fits are compared, the crystal-field model (the combination of the free-ion Hamiltonian with one-body crystal-field operators) works rather well for the 4f series, but shows much greater deviations for 5f ions. Of course, Pa^{4+} is tetravalent and is subject to a considerably larger crystal-field than Ce^{3+} . In addition the greater spatial extent of the 5f wavefunction could result in greater covalent bonding with the Cl^- ligands. As expected the spin-orbit coupling constant for the 6d configuration in Pa^{4+} is much larger than for the 5d configuration in Ce^{3+} , although it appears that $10Dq$ (the crystal-field splitting of one d electron in an octahedral field, defined as the difference between the energies of the e_{2g} and t_{2g} orbitals in the absence of spin-orbit coupling) is larger for $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ than for $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$. However this latter number is uncertain and the differences in $10Dq$ do not appear to be significantly different.

Comparison of An^{3+} and Ln^{3+} in LaCl_3

Carnall [15] has recently published a compendium of the data for $\text{An}^{3+}/\text{LaCl}_3$ and his analysis of these data. He carried out a new energy level analysis for the entire series where data are available (from U^{3+} through Es^{3+}).

The values of σ for the actinides (which are a measure of the quality of the fits) are between 20 - 22 cm^{-1} . This compares with values of σ for the lanthanides on the order of 10 cm^{-1} . Carnall was able to arrive at a consistent analysis by assuming the parameters of the principal interactions showed uniform trends as a function of atomic number. The exception to this trend occurred at the beginning of the series where the parameters for U^{3+} (free ion as well as crystal field) were not consistent with the data for the heavier ions. The crystal-field parameters for the actinides are approximately twice as large as those for the lanthanides, except for B_0^2 (not including U^{3+}) where the values for the lighter actinides are of the same order as those in the lanthanide series. Carnall also compared the splittings of the ground terms of each member of the lanthanide and actinide series with the same number of f electrons. For most cases the ordering of the crystal field states (labeled by the quantum number μ where $J_z = \mu(\text{mod } q)[10]$) is the same in both the lanthanide and actinide ions.

The total crystal-field strength has been defined by Auzel and Malta [16] as

$$N'_v = \frac{N_v}{2\pi} \left[\sum_{k,q} (B_q^k)^2 / (2k+1) \right]^{1/2}$$

with N'_v in units of cm^{-1} .

A comparison of the values of N'_v for the lanthanide and actinide series is given in Figure 4. It appears the strength of the crystal field in the actinides is about a factor of two larger than in the lanthanides. Note that in the lanthanides the crystal-field strength for the latter half of the series is less than in the first half of the series, but no trend is discernible in the actinides. Of course there are relatively sparse data for the actinides, so this generalization must be treated with caution.

f-Element Organometallic Compounds

Although actinide organometallic chemistry is a very active area of interest, only a few detailed optical or magnetic measurements have been reported on trivalent actinide organometallic compounds. For this review two sets of compounds have been chosen; Cp_3^-Th , Cp_3^-Ce and $\text{Cp}_3^-\text{U.L}$, $\text{Cp}_3^-\text{Nd.L}$ where $\text{L} = \text{CNC}(\text{CH}_3)_3$ and $\text{Cp}'' = \eta^5 - \text{C}_5\text{H}_3(\text{SiMe}_3)_2$ [17-19]. Low temperature electron paramagnetic resonance (epr) and magnetic susceptibility data measured as a function of temperature are available for this series of compounds. The data for the $\text{Cp}_3^-\text{U.L}$, $\text{Cp}_3^-\text{Nd.L}$ pair are given in Table 3. It is clear that the ground crystal-field states are similar for both the Nd and U compounds. The difference between the room temperature magnetic susceptibilities can be explained by a larger crystal-field splitting in the uranium compound as compared to the Nd compound.

For the Th^{3+} free ion, the ground configuration is $5f^1$ with the $6d^1$ configuration at $\sim 10,000 \text{ cm}^{-1}$. In compounds however the $6d$ configuration is stabilized with respect to the $5f$ configuration, and in Cp_3^-Th it becomes the ground configuration [17]. For the Ce^{3+} free ion, the ground configuration is $4f^1$ and the $5d^1$ excited configuration is at $\sim 50,000 \text{ cm}^{-1}$. In Cp_3^-Ce the start of the $5d$ configuration is at $\sim 17,000 \text{ cm}^{-1}$. Table 4 shows the epr data for Cp_3^-Ce , Cp_3^-Th , Cp_3Zr , and $(\text{MeCp})_3\text{Zr}$ ($\text{Cp} = \eta^5 - \text{C}_5\text{H}_5$, $\text{MeCp} = \eta^5 - \text{C}_5\text{H}_4\text{CH}_3$) [18,19]. Clearly the g values for the ground state of Th Cp_3^- match those of Cp_3Zr and $(\text{MeCp})_3\text{Zr}$ much more closely than those of Cp_3^-Ce which verifies the assignment of the ground state in the Th compound as the d_{z^2} orbital.

Comparison of $\text{Eu}^{3+}/\text{ThO}_2$ and $\text{Am}^{3+}/\text{ThO}_2$

Optical spectra for $\text{Eu}^{3+}/\text{ThO}_2$ and $\text{Am}^{3+}/\text{ThO}_2$ have recently been reported [20] and provide another host matrix in which to compare the effects of the crystal field on the f^6 configuration. Table 5 shows the values of the parameters found from the analysis. The larger crystal field found for the actinides and especially for the ThO_2 matrix causes extensive J mixing in Am^{3+} . This is in contrast to Eu^{3+} where the states show rather pure L-S coupling. Again the values of the parameter N_{ν} show that the total crystal field strength in $\text{Am}^{3+}/\text{ThO}_2$ is 2.4 times greater than that in $\text{Eu}^{3+}/\text{ThO}_2$.

The f^7 configuration

The ground state wavefunction of Gd^{3+} ($4f^7$) is an almost pure $^8S_{7/2}$ state which, because $L = 0$, should undergo no splitting in a crystalline field. However, for this ion and ions of the d transition metals, small splittings are observed. Much work has been done on various higher-order interactions which can cause these splittings but the mechanisms are still not well understood. For the Gd^{3+} ion in various hosts, the extent of the ground state splittings is on the order of 0.5 cm^{-1} or less. For Cm^{3+} in various host crystals the ground state splittings are on the order of 10 cm^{-1} [21]. Some data from epr measurements on Cm^{3+} in various crystals compared with Gd^{3+} are shown in Table 6. The reason for the rather large differences in the splittings of the ground term between Gd^{3+} and Cm^{3+} can be explained by the large spin-orbit coupling in Cm^{3+} . Table 7 shows the free-ion wavefunctions for Gd^{3+} and Cm^{3+} . The Cm^{3+} free-ion wavefunction consists of 50 L-S terms of which those with $L > 1$ can split in a crystal field. It has been shown that by adding up all these terms the calculated splittings found for Cm^{3+} agree quite well with the measured values. This is not

true for Gd^{3+} , as a large number of interactions of approximately the same magnitude contribute to the observed splittings.

Sytsma *et al.* [22] have recently completed an analysis of the optical spectra of Gd^{3+} and Cm^{3+} in the tetragonal host crystal $LuPO_4$. Earlier work on the epr of $Cm^{3+}/LuPO_4$ had been analyzed in terms of a total ground term splitting of approximately 11 cm^{-1} . The optical analysis confirms this splitting and Sytsma *et al.* obtained crystal-field parameters for both Gd^{3+} and Cm^{3+} in $LuPO_4$. The parameters obtained from the optical analyses are shown in Table 8. Again we see that N_v is about twice as large for Cm^{3+} as found for Gd^{3+} .

Conclusion

The optical data available for f^n ions of the same oxidation state have been reviewed. Using the Auzel and Malta parameter N_v as a measure of the strength of the crystal field, one finds the actinide crystal field is approximately twice that of the corresponding lanthanide ion. From an electrostatic model the crystal-field parameters B_q^k can be written as [24]

$$B_q^k = A_q^k \langle r^k \rangle$$

where the value of A_q^k depends on the type of electrostatic model assumed. Since the ionic radii of the actinide and lanthanide ions are similar, it is expected that the values of A_q^k for ions of the lanthanide and actinide series should be similar. Thus qualitatively, one can attribute the larger crystal-field interactions in the actinide series to the more extended nature of the 5f wavefunctions as given by $\langle r^k \rangle$. However this is a gross oversimplification as this model does not include f-orbital covalency, whose effects are clearly observed in epr experiments. For example, a large superhyperfine structure has been reported for PuF_8^{5-} (Pu^{3+} in

the cubic site of CaF_2 [25]. The incorporation of covalency effects into a ligand field model and its application to the actinides needs further implementation.

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Parameter	Nd ³⁺ (4f ³) ^a	Er ³⁺ (4f ¹¹) ^a	U ³⁺ (5f ³) ^b	Fm ³⁺ (5f ¹¹) ^b
F ²	71866	98203	39611	65850
F ²	52132	69647	32960	52044
F ⁶	35473	49087	23084	37756
ζ	880	2370	1626	4326
α	22.1	15.9	29.26	30
β	-650	-632	-824.6	-600
γ	1586	2017	1093	450
T ²	377	300	306	100
T ³	40	48	42	45
T ⁴	63	18	188	50
T ⁶	-292	-342	-242	-300
T ⁷	358	214	447	640
T ⁸	354	449	300	400
M ⁰	1.97	4.5	.672	1.587
M ²	1.1	2.52	.372	.878
M ⁴	.75	1.71	.258	.612
P ²	255	667	1216	600
P ⁴	191	500	608	300
P ⁶	128	334	121.6	60
B ₀ ²	107	216	287	306
B ₀ ⁴	-342	-271	-662	-1062
B ₀ ⁶	-677	-411	-1340	-1441
B ₆ ⁶	466	272	1070	941

^aFrom reference 15.

^bFrom reference 26.

TABLE 1: Energy level parameters for representative lanthanide and actinide ions diluted in LaCl₃. All values in cm⁻¹.

Crystal field levels and g value	Pa ⁴⁺ Energy Levels ^a (Exp)	Pa ⁴⁺ Energy Levels ^a (Calc)	Ce ³⁺ Energy Levels ^b (Exp)	Ce ³⁺ Energy Levels ^b (Calc)
5d or 6d (Γ_{8g}) (cm ⁻¹)	40000	40000 ^c	>50000	50000 ^d
5d or 6d (Γ_{7g}) (cm ⁻¹)	23000	23000	29435	29435
5d or 6d (Γ_{8g}) (cm ⁻¹)	19954	19954	28196	28196
² F _{7/2} (Γ_{6u}) (cm ⁻¹)	8173±3	8173 ^e	3085.6± 2	3085.6 ^f
² F _{7/2} (Γ_{8u}) (cm ⁻¹)	7272±3	7272	2688.8± 2	2688.8
² F _{7/2} (Γ_{7u}) (cm ⁻¹)	5250±50	5539	2159±50	2160.1
² F _{5/2} Γ_{8u} (cm ⁻¹)	2108±1	2108	598.5±2	598.5
² F _{5/2} Γ_{7u} (cm ⁻¹)	0	0	0	0
$g_{\Gamma_{7u}}$	-1.141±.002	-.953	-1.266	-1.255

^areferences 12 and 13

^breferences 11 and 14

^c10Dq = 18600 cm⁻¹, ζ_{6d} = 1856.5 cm⁻¹, E_{ave} = 28582 cm⁻¹

^d10Dq = 21318 cm⁻¹, ζ_{5d} = 796.8 cm⁻¹, E_{ave} = 37165 cm⁻¹

^eB₀⁴ = 6945.3 cm⁻¹, B₀⁶ = -162.7 cm⁻¹, ζ_{5f} = 1539.6 cm⁻¹

^fB₀⁴ = 2219.1 cm⁻¹, B₀⁶ = -254.9 cm⁻¹, ζ_{4f} = 622.7 cm⁻¹

TABLE 2: Experimental and calculated energy levels and ground state g values for Ce³⁺/Cs₂NaYCl₆ and Pa⁴⁺/Cs₂ZrCl₆

Compound	g_1^a	g_2^a	g_3^a	$g_{ave}(epr)^a$	$g_{ave}(suscept.)^b$	$\mu_{eff}(BM)^c$
$Cp_3\bar{Nd}.CNC(CH_3)_3$		2.231	2.095	.856	1.73	1.66 3.85
$Cp_3\bar{U}.CNC(CH_3)_3$	2.463	1.739	<.7	$1.39 < g < 1.63$	1.69	3.13

^aAt ~ 10K

^bTemp. range 5–10K, $S=1/2$

^cTemp. range 200–300K

TABLE 3. Magnetic susceptibility and electron paramagnetic resonance data for $Cp_3\bar{M}.CNC(CH_3)_3$ (M=Nd,U). The data are from reference 19.

	Config.	g_{\parallel}	g_{\perp}	g_{ave}	Temp(K)	Ref.
Cp_3Th in MCH ^a	6d ¹			1.910±.001	300	17
Cp_3Th in MCH	6d ¹	1.9725±.001	1.879±.001	1.910 ^b	10-110	17
Cp_3Th powder	6d ¹	1.972±.001	1.878±.001	1.909 ^b	10-300	17
Cp_3Zr in 2-MeTHF ^c	4d ¹	1.999	1.970	1.980 ^b	100	19
Cp_3Zr in 2-MeTHF	4d ¹			1.977	298	19
$(CH_3Cp)_3Zr$ in 2-MeTHF	4d ¹	1.999	1.969	1.979 ^b	100	19
$(CH_3Cp)_3Zr$ in 2-MeTHF	4d ¹			1.977	298	19
Cp_3Ce powder	4f ¹	2.77	2.39	2.52 ^b	5	18

^aMCH = methylcyclohexane

^bCalculated from $1/3 (g_{\parallel} + 2g_{\perp})$

^c2-MeThF = 2-methyltetrahydrofuran

TABLE 4. EPR Data for Various f¹ or d¹ Organometallic Compounds

Parameters (cm ⁻¹)	Eu ³⁺ /ThO ₂ ^a	Am ³⁺ /ThO ₂ ^b
F ²	[80335.2] ^c	48038.0(140.2) ^d
F ⁴	[58953.9]	39684.2(212.9)
F ⁶	[41636.6]	29514.1(171.4)
ζ	1337.3(7.1)	2511.1(27.0)
α	[16.8]	33.2(8.6)
β	[-640]	[-660]
γ	[1750]	[1000]
T ²	[370]	[200]
T ³	[40]	[50]
T ⁴	[40]	[40]
T ⁶	[-330]	[-360]
T ⁷	[380]	[390]
T ⁸	[370]	[340]
M ⁰	[2.38]	[.99]
M ²	[1.33]	[.55]
M ⁴	[.90]	[.38]
P ²	[245]	[850]
P ⁴	[183.8]	[637.5]
P ⁶	[122.5]	[425]
B ₀ ⁴	-2780.2(32.2)	-6731.3(96.0)
B ₀ ⁶	266.0(26.3)	713.6(115)
N _v	1212	2945

^a17 experimental levels, rms deviation 18.0 cm⁻¹.

^b17 experimental levels, rms deviation 47.3 cm⁻¹.

^cAll parameter values in [] held fixed in the fitting procedure.

^dNumber in () is the standard deviation of the parameter.

TABLE 5: Spectroscopic parameters for Eu³⁺ and Am³⁺ diluted in ThO₂ From Reference 20.

Host	Lattice Constant	Gd ³⁺	Cm ³⁺
CeO ₂	5.41Å	.0653 cm ⁻¹	17.8 cm ⁻¹
ThO ₂	5.60	.06645	15.5
CaF ₂	5.46	.0578	13.4
SrF ₂	5.80	.0501	11.2
SrCl ₂	7.00	.0198	5.13

TABLE 6. Comparison of the ground state crystal-field splittings of Gd³⁺ and Cm³⁺ in cubic crystals.

L-S Term	Gd ³⁺		Cm ³⁺	
	Component	Percentage	Component	Percentage
⁸ S	-.9857	97.16	.8859	78.48
⁶ P	-.1666	2.77	-.4232	17.91
⁴ D ₆	-.0146	.0213	-.1052	1.107
⁴ D ₁	-0.0144	.0207	-.1039	1.079
⁶ D	.0127	.0161	.0926	.857
⁴ D ₄	.0031	.96x10 ⁻³	.0205	42.0x10 ⁻³
⁴ F ₄	.0020	.40x10 ⁻³	.0409	.167
² F ₆	.0016	.26x10 ⁻³	.0322	.103
⁶ F	-.0011	.12x10 ⁻³	-.0227	51.5x10 ⁻³
⁴ D ₃	-.0011	.12x10 ⁻³	-.0226	51.1x10 ⁻³

TABLE 7. Free-ion wavefunctions for Gd³⁺ and Cm³⁺. Parameters from reference 22.

Parameter	Gd ³⁺ ^a	Cm ³⁺ ^b
F ²	84075	54669
F ⁴	61411	44760
F ⁶	44426	33021
ζ	1494	2867.7
α	[18.9] ^c	30.3
β	[-600]	-982
γ	[1575]	749
T ²	[300]	[200]
T ³	[42]	[50]
T ⁴	[62]	[40]
T ⁶	[-295]	[-360]
T ⁷	[350]	[390]
T ⁸	[310]	[340]
M ⁰	[3.22]	[1.09]
M ²	[1.80]	[.61]
M ⁴	[1.22]	[.41]
P ²	[676]	[912]
P ⁴	[507]	[684]
P ⁶	[338]	[456]
B ₀ ²	168.6	442.7
B ₀ ⁴	220.1	304.1
B ₄ ⁴	-1034.2	-1980.3
B ₀ ⁶	-733.4	-2880.1
B ₄ ⁶	960.6	881.3
N _v	657.3	1295.6

^a44 experimental levels, $\sigma = 15.1 \text{ cm}^{-1}$

^b60 experimental levels, $\sigma = 30.8 \text{ cm}^{-1}$

^cValues in [] held fixed

TABLE 8: Energy level parameters for Gd³⁺ and Cm³⁺ diluted in LuPO₄. From Reference 22. All values are in cm^{-1} .

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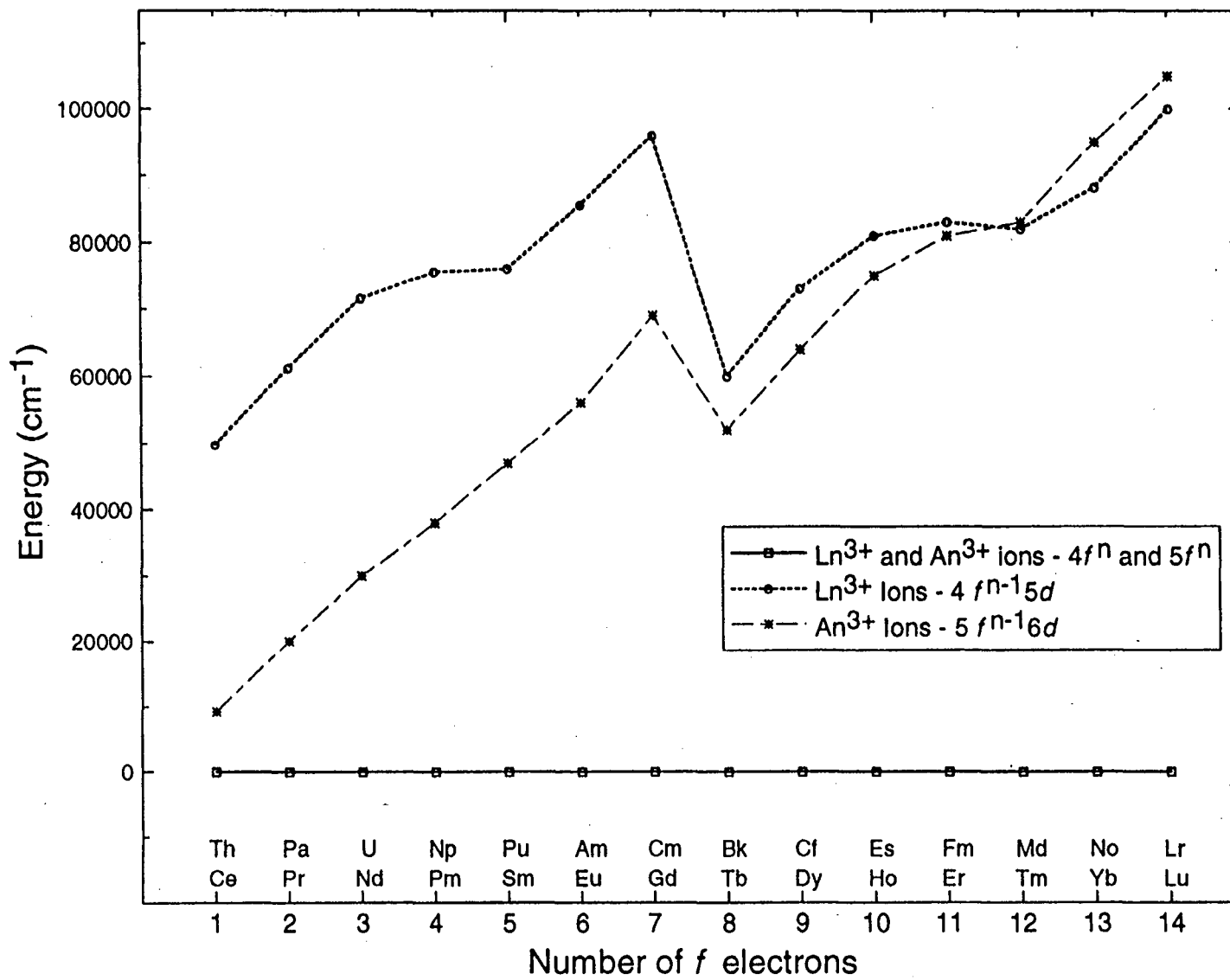


Fig. 1

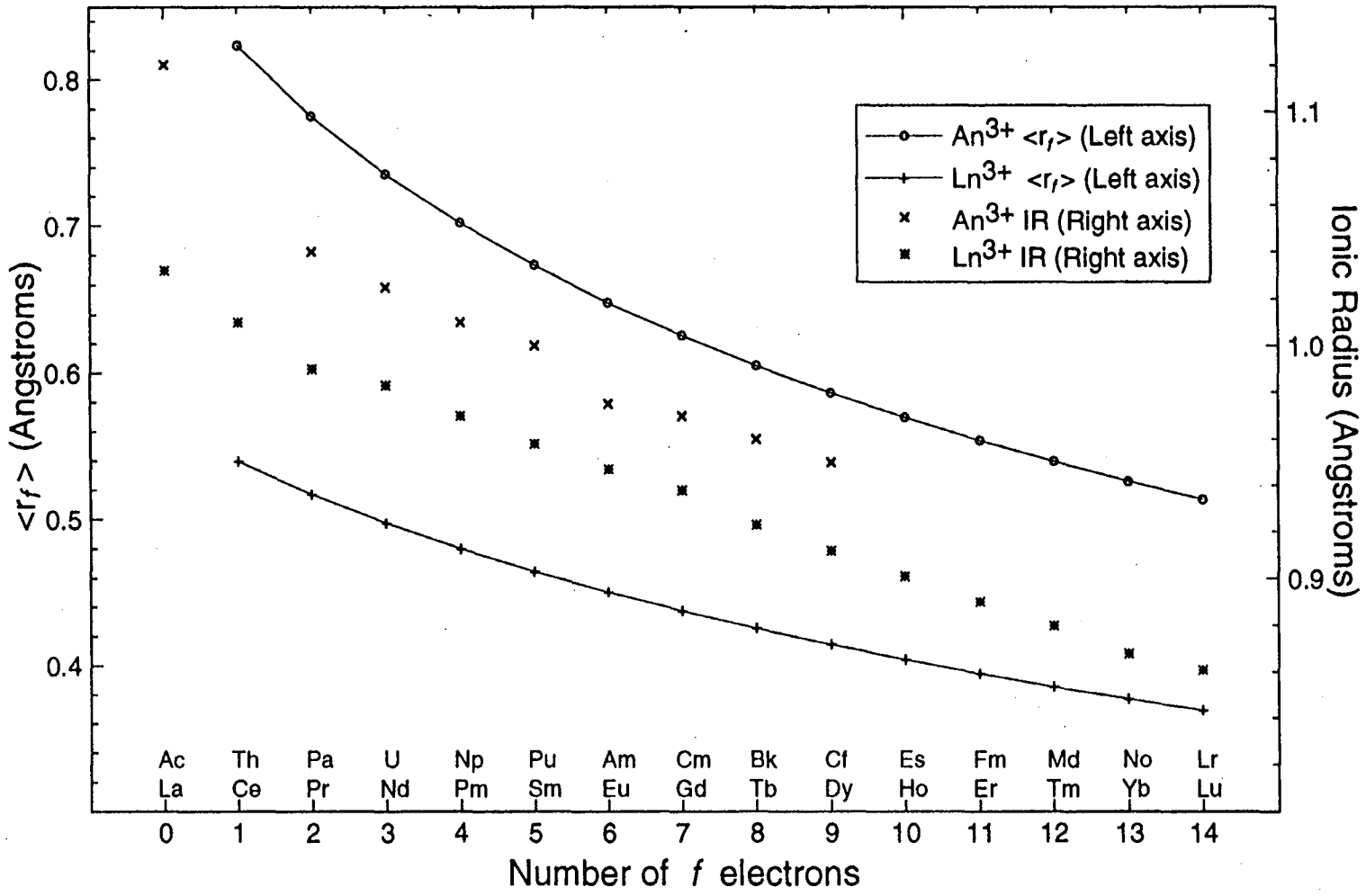


Fig. 2

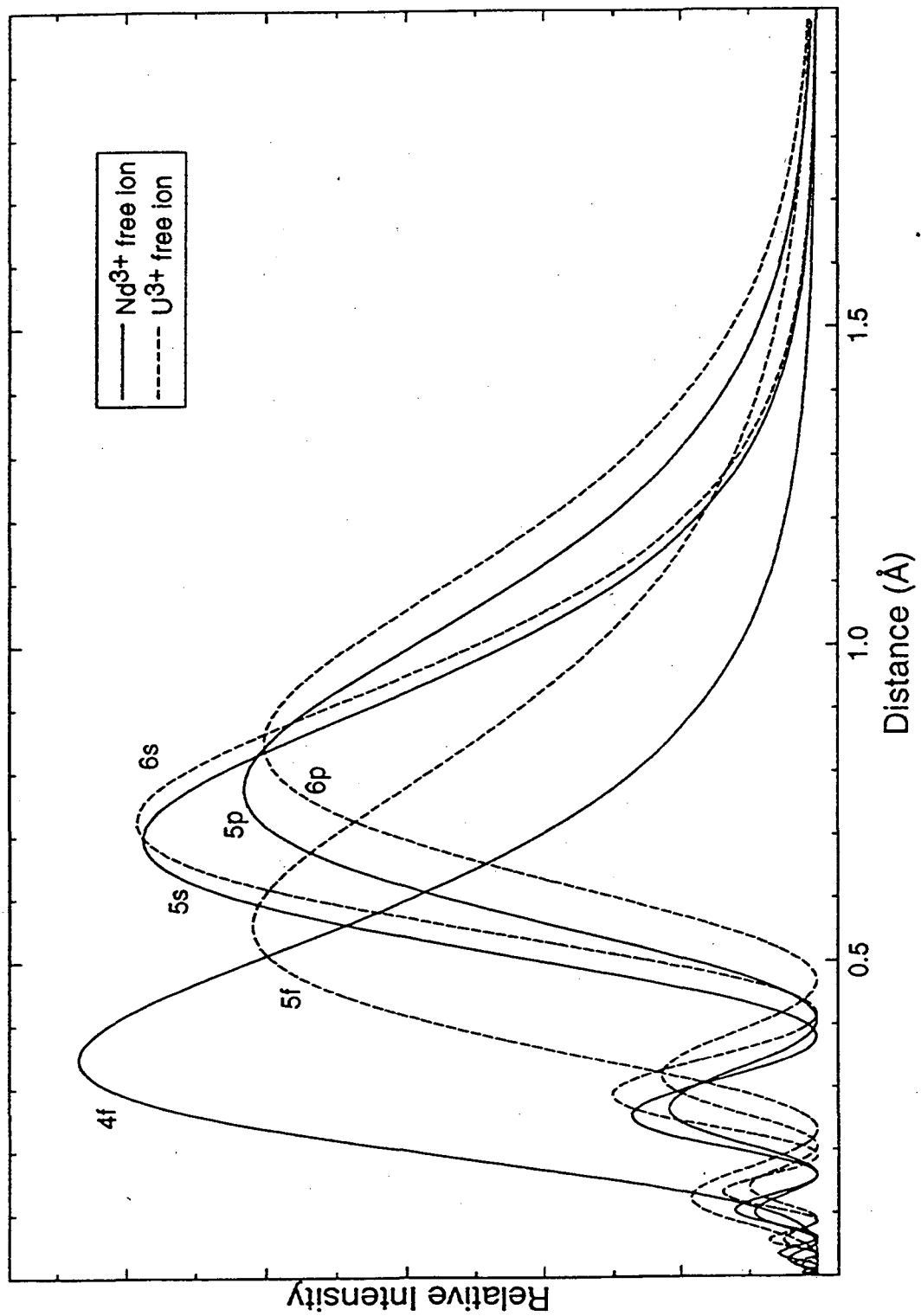


Fig. 3

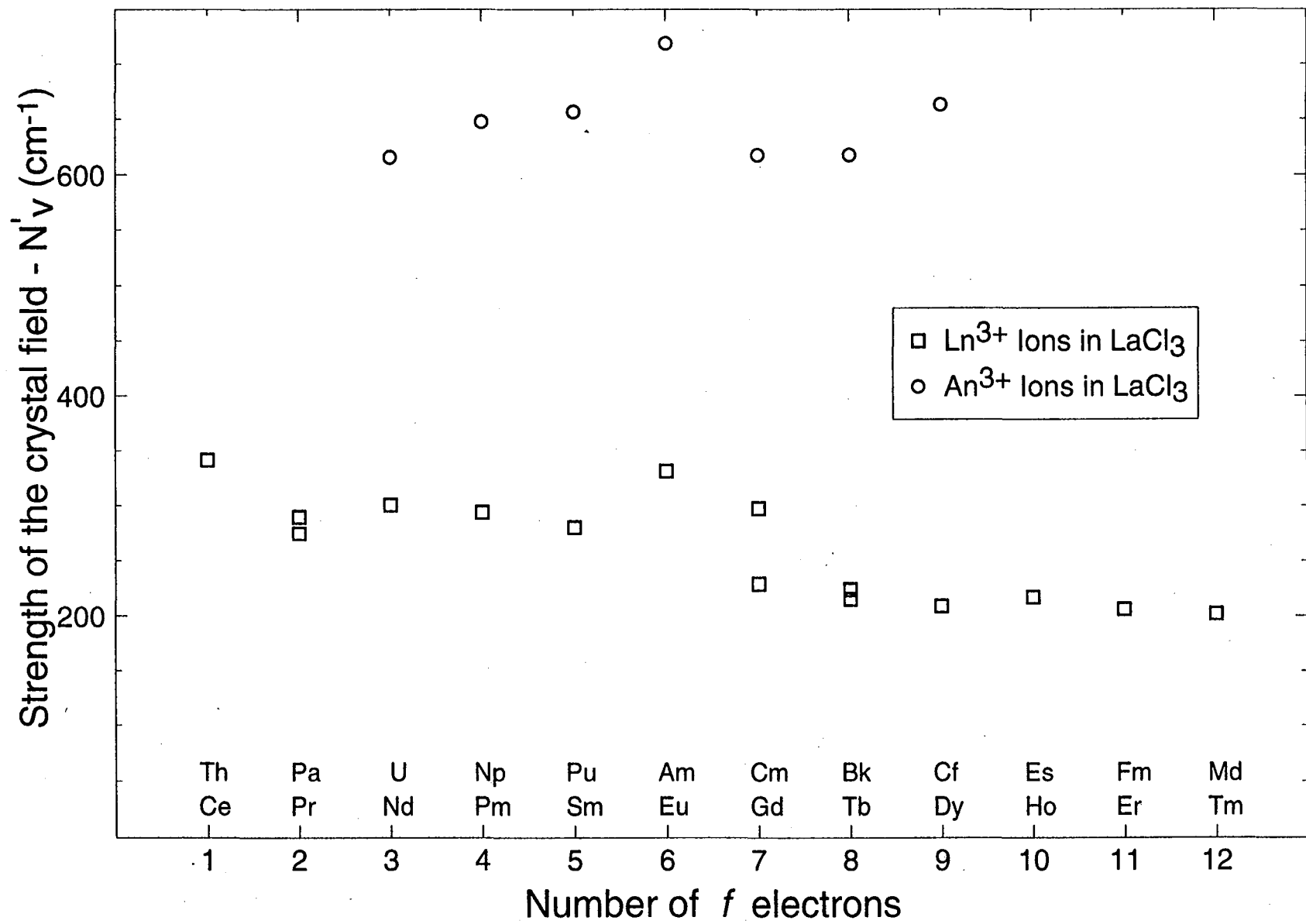


Fig. 4

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