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ABSTRACT. - Magnetic and optical studies of both the ground and excited f and d configurations of the one electron ions Ce^{3+}, Th^{3+}, and Pa^{4+} in single crystals and compounds are reviewed.

Introduction

At the beginning of both the 4f and 5f electron series, the possible electron configurations for atoms or ions with one electron outside the xenon or radon core are very close in energy. For example the Cs atom, [Xe] core plus one electron, has eight different one electron configurations within 25,000 cm^{-1} [1]. As the degree of ionization increases for the one electron (outside the closed shells) ions, the 4f or 5f configuration becomes stabilized with respect to the other possible configurations. The free ion data for BaII (Ba^{1+}) to PrV (Pr^{4+}) and RaII (Ra^{1+}) to UVI (U^{5+}) are shown in Figs. 1 and 2 [2,3].

Of the one-electron ions shown in Figs. 1 and 2, Ce^{3+}, Pr^{4+}, Th^{3+}, Pa^{4+}, and U^{5+} form accessible chemical compounds. Pa^{4+} is a stable oxidation state for element 91, but the naturally occurring isotope ^{231}Pa is part of the ^{235}U decay chain

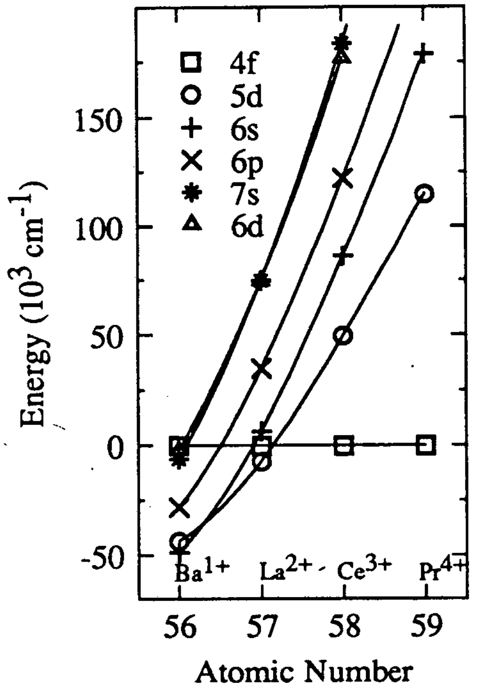

Figure 1.

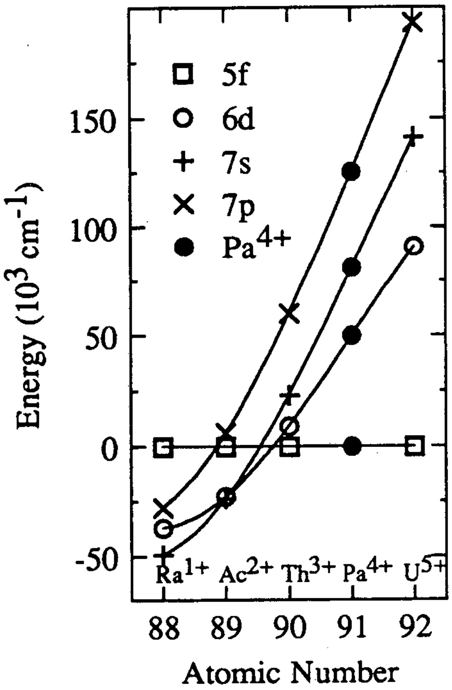

Figure 2.

Figure 1. Relative energies of the lowest levels of various one electron configurations for a number of one electron ions at the beginning of the lanthanide series. From Refs. 1 and 2.

Figure 2. Relative energies of the lowest levels of various one electron configurations for a number of one electron ions at the beginning of the actinide series. From Ref. 3. The points for Pa^{4+} are interpolated.

and handling this element and its compounds is difficult, primarily due to the radioactivity of the ^{231}Pa daughters. There is only one known structurally characterized compound of Th^{3+} [4]. La^{2+} has been stabilized only in fluorite type crystals (CaF_2 and $SrCl_2$), but little optical data is available on this ion [5-7]. For compounds of PrV (Pr^{4+}) or UVI (U^{5+}) only the ground 4f or 5f configurations are accessible by conventional optical techniques. The purpose of this paper is to review recent studies of the optical and/or magnetic data of Ce^{3+}, Th^{3+}, and Pa^{4+} for which information is available on both the ground and the first excited configurations.

For f^N compounds, the excited d configurations are important because admixtures of these configurations permit the observation of electric dipole transitions within the f^N configuration. Formally, electric dipole, one photon transitions are forbidden. The mechanism by which these optical transitions become weakly allowed is from the mixing by the odd components of the crystal field of higher-lying configurations of opposite parity ($f^{N-1}d$ or $f^{N-1}g$) into the ground f^N configuration. The Judd-Ofelt theory was developed originally to quantitatively calculate the intensities of these transitions [8,9]. An essential part of the original development of the theory was the use of the closure approximation in which it is assumed the average energies of the opposite parity configurations are so high in energy compared to the overall width of the configurations that the levels of each of the configurations can be treated as degenerate. The approximations of the Judd-Ofelt theory were extended by Axe to cover two photon processes such as electronic Raman scattering (ERS) and two photon absorption [10].

Although configurations of the type $f^{N-1}g$ are certainly much higher in energy than $f^{N-1}d$ configurations, a number of one and two photon intensity experiments involving f^N ions in the ground state are most readily analyzed by the inclusion of g orbital effects [11-14]. If the d configuration is much lower in energy than other excited configurations, then the contribution to the intensities of an f^N ion from this isolated low-lying configuration of opposite parity should be the most significant. Recent ERS and absorption experiments on the $4f^1$ and $5d^1$ configurations in $Ce^{3+}/LuPO_4$ have been analyzed on this basis [15,16].

Ce^{3+} Spectroscopy

There have been a large number of studies reported for Ce^{3+} as an impurity in various host matrices. In most cases, only some of the levels in the 5d configuration have been located. The energy levels of Ce^{3+} in some oxide and fluoride hosts are shown in Fig. 3 [15, 17-20]. There are several generalizations that can be made from this figure. First of all, the major splitting of the $4f^1$ level is due to spin-orbit coupling and this does not vary much from crystal host to crystal

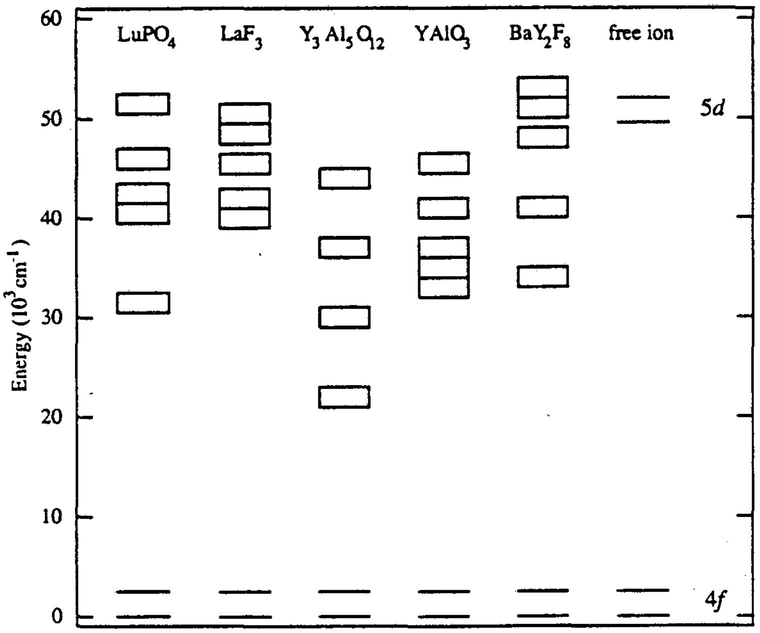

Figure. 3. Approximate 4f and 5d crystal field energy levels for Ce^{3+} in several different crystals. Only four of the five 5d levels are observed below the band gap of $Y_3Al_5O_{12}$ which begins at ~50,000 cm^{-1}. References: $LuPO_4$ [15]; LaF_3 [17]; $Y_3Al_5O_{12}$ [18]; $YAlO_3$ [19]; BaY_2F_8 [20].

host or from the free-ion data. Secondly, for the $5d^1$ excited configuration, the crystal field is the dominant term, and there is a large variation in the total splitting of the $5d^1$ configuration and in the energies of the levels. It is also clear from these energy level diagrams that the difference between the centers of gravity of $5d^1$ and $4f^1$ configurations of Ce^{3+} is lowered dramatically in crystals as compared to the free ion. This difference varies from crystal to crystal. Blasse has reviewed briefly the crystal field shifts and splittings for the Ce^{3+} $5d^1$ excited configuration in several host lattices [21]. He noted particularly the large 5d level shifts to lower energy for covalent crystals such as $Ce^{3+}/CsCdBr_3$, Ce^{3+}/CaS, and Ce^{3+}/Y_2O_2S. For example, for Ce^{3+} in CaS, the lowest 5d level is at 21,073 cm^{-1} [22].

Aull and Jenssen have presented a phenomenological model in which they list and calculate the various contributions to the energy and splittings of the 5d configuration for a CeF_6^{3-} complex [23]. In addition they have measured the emission and optical absorption spectra of Ce^{3+} in a number of fluoride elpasolites and compared in detail the data for Ce^{3+}/Rb_2NaYF_6 and $Ce/YLiF_4$ [24]. From their emission data for Ce^{3+}/Rb_2NaYF_6 they derive a very large total splitting for the $4f^1$ levels of ~ 5800 cm^{-1}, much greater than for $Ce^{3+}/YLiF_4$. However the crystal field splitting for the $5d^1$ levels in Ce^{3+}/Rb_2NaYF_6 is given as 10 Dq = 18,200 cm^{-1}. These results are somewhat in conflict with the data for $Cs_2NaCeCl_6$ where the total 4f splittings is 3048 cm^{-1} [25] and Schwartz and Schatz have found that for the $5d^1$ configuration in Ce^{3+}/Cs_2NaYCl_6, 10 Dq $\geq$ 20,000 cm^{-1} [26]. In the latter work, the 5d optical data were obtained with Ce^{3+} doped into a lattice with a smaller lattice constant than the pure compound, which results in a larger value of 10 Dq than would be expected for $Cs_2NaCeCl_6$. Nevertheless, the discrepancies between the reported $4f^1$ splittings and the $5d^1$ splittings of Ce^{3+}/Rb_2NaYF_6 and $Cs_2NaCeCl_6$ (or Ce^{3+}/Cs_2NaYCl_6) are so large that further investigation is warranted.

A number of investigations of various types have been reported for the Ce^{3+}/CaF_2 system [27-30]. The Ce^{3+} ion may go into a number of different sites in the fluorite lattice depending on the concentration of the Ce^{3+} ion, and the presence (or absence) of other impurities. In a very interesting experiment, Gayen and Hamilton [31] reported the two-photon excitation of the lowest 4f-5d transition for the tetragonal site (C_{4v}) of Ce^{3+}/CaF_2, where the Ce^{3+} ion replaces a Ca^{2+} and a charge compensating F^- is at the center of the next cube of F^- ions. The two photon electric dipole transition between 4f and 5d levels is formally forbidden, but the absence of a center of symmetry allows odd components of the crystal field to mix into the ground 4f level configurations of opposite parity. This mechanism is the same as that discussed earlier for one photon electric dipole transitions between levels of an f^N configuration. Gayen and Hamilton have measured the peak cross section for this two photon process and conclude there is significant crystal field mixing of configurations of opposite parity. Subsequently they have presented a calculation of the 4f-5d two photon cross section based on the Judd-Ofelt-Axe theory [32].

Williams, et al. have analyzed the $4f^1$ and the excited $5d^1$ configurations of $Ce^{3+}/LuPO_4$ by ERS for the 4f levels and absorption spectroscopy for the 5d levels [15]. Because the 5d configuration is so low in energy (the first 5d level is at ~ 30,000 cm^{-1} and the total spread of the $5d^1$ configuration is approximately 20,000 cm^{-1}), the closure approximation used in the Judd-Ofelt theory was not adequate. The relative intensities of ERS were calculated by explicitly evaluating the sum over the intermediate 5d configuration using the wavefunctions from a crystal field fit and the experimental $5d^1$ energies. This explicit calculation reproduced the observed relative intensities more accurately than the standard theory as expected.

Williams, et al. [16] then measured the oscillator strengths for the optical transitions from the ground 4f level in $Ce^{3+}/LuPO_4$ to all the $5d^1$ levels and the absolute cross sections for ERS between the levels of the $4f^1$ configuration. The measured oscillator strengths were approximately 2.5 to 20 times smaller than the corresponding theoretical values and the absolute cross sections for ERS were also significantly smaller than expected. The intermediate states used in the calculation of the ERS cross sections are the states of the $5d^1$ configuration. When the electric dipole matrix elements between the 4f and 5d states were empirically corrected by using a factor given by the square root of the ratio of the measured to the calculated f to d oscillator strengths, the agreement between the observed and calculated Raman differential cross sections for $Ce^{3+}/LuPO_4$ was excellent. Some data from Williams, et al. are shown in Table I.

Table I. Observed and calculated electronic Raman differential scattering cross sections for Ce^{3+} in $LuPO_4$. From Ref. 16

Raman Transition Δ (cm^{-1})	10^{30} ($d\sigma/d\Omega$) (cm^2/sr) Observed	Calculated with weighted 5d wave functions
240	0.3	2.8
429	7.4	7.8
2179	3.25	2.9
2221	1.9	1.9
2620	1.35	1.9
2676	0.55	0.5

This calculation and the satisfying results listed in Table I suggest that for the ERS intensities in $Ce^{3+}/LuPO_4$, the $5d^1$ configuration is indeed the major factor determining the scattering cross sections. However this may not be true in general, and, as mentioned earlier, g type orbitals may play a major role.

Williams, et al. correlated the reduction of the oscillator strengths with a reduction of the radial integral ⟨4f|r|5d⟩ for Ce^{3+} in a number of crystals [16]. A plot taken from Williams [33] of the ratio of observed over calculated oscillator strength vs the average Ce^{3+}-ligand distance is shown in Fig. 4. The reduction of the 4f → 5d oscillator strength with a decrease in the Ce^{3+}-ligand distance has been attributed to greater 5d-ligand overlap.

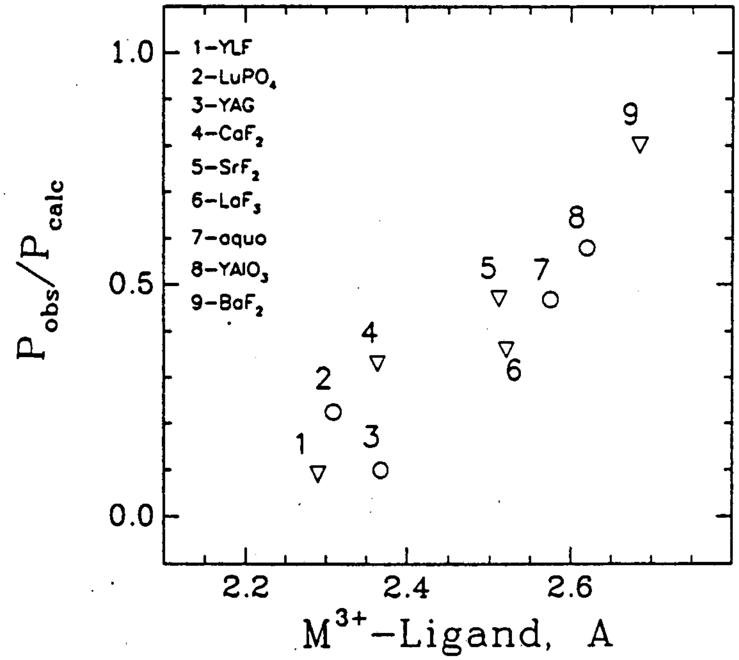

Figure 4. Ratio of observed over calculated oscillator strength vs. the average M^{3+}-ligand distance. Oxide crystals are marked by circles, fluoride crystals are marked by inverted triangles. From Williams, Ref. 33.

One consequence of the relatively low energy of the 5d configuration in $Ce^{3+}/LuPO_4$ is that laser sources may be conveniently tuned close to the threshold of the first 5d level. Williams, et al. [15] reported the results of such an experiment using the frequency-tripled Nd-YAG output. The intensity I for ERS may be written as

$$I \propto \omega_s^3 \omega_\ell \left| \sum_n \frac{\langle i|e\vec{r}|n\rangle\langle n|e\vec{r}|f\rangle}{\omega_\ell - \omega_n} \right|^2 \qquad (1)$$

where $e\vec{r}$ is the electric dipole operator, ω_s and ω_ℓ are the angular frequencies of the scattered and incident laser radiation, and i and f are the initial and final states of the ground configuration. The intermediate states n are from configurations of opposite parity to the f^N ground configuration. For $Ce^{3+}/LuPO_4$ the lowest 5d level is at 30468 cm^{-1}. The output of a frequency-tripled Nd-YAG laser is at 28191.5 cm^{-1}. Therefore from the above equation the enhancement of ERS relative to the Ar ion laser line at 514.5 nm (19429.7 cm^{-1}) is

$$\left(\frac{\omega_{5d} - 28191.5}{\omega_{5d} - 19429.7}\right)^2 \approx 25.$$

There is an additional factor of ~ 4.5 from $\omega_s{}^3\omega_\ell$ term in Eq. 1. Experimentally, Williams, et al. measured enhancements on the order of 100 [15]. Piehler and Edelstein have used resonances with the 5d level to enhance four-wave mixing processes in $Ce^{3+}/LuPO_4$ [34].

Th^{3+} and Pa^{4+} Spectroscopy and Magnetic Measurements

In the actinide series only the Th^{3+} and Pa^{4+} ions have both the 5f and 6d configurations accessible by conventional optical techniques. Axe[35] developed the techniques to grow single crystals of Cs_2ZrCl_6 and incorporated the Pa^{4+} ion at the Zr ion site (O_h symmetry) as an impurity. He and coworkers [36] measured the EPR spectrum of the ground Γ_7 state and the energy levels of the $5f^1$ configuration in the near-infrared region. From these data the crystal field parameters and the spin-orbit coupling constant of the $5f^1$ configuration of Pa^{4+} in Cs_2ZrCl_6 were obtained. Axe also scanned the visible region of the Pa^{4+}/Cs_2ZrCl_6 sample and observed strong absorption bands but did no analysis.

Subsequently, Edelstein, et al. [37] and Brown, et al. [38] measured and analyzed the near-infrared spectrum of a number of Pa^{4+} compounds. In 1984, Naik and Krupa [39] observed visible fluorescence spectra from the $6d^1$ configuration to the $5f^1$ levels in the $Pa^{4+}/ThBr_4$ system. The optical and EPR spectra of this sample had been reported earlier [40]. Edelstein, et al. [41] presented an analysis of the absorption and fluorescence spectra of the $6d^1$ configuration of $Pa^{4+}/ThBr_4$ and of the absorption spectrum of solutions of the PaX_6^{2-} ion (X = Cl, Br). From this work the spin-orbit coupling constant of the 6d electron plus a limit on the minimum splitting of the 6d configuration in these systems was obtained. In addition it was noted that there was a significant decrease in the relative centers of gravity of the $5f^1$ and $6d^1$ configurations (~25,000 cm^{-1}) between the Pa^{4+} free ion and the Pa^{4+} ion in these crystal matrices.

Piehler, Kot, and Edelstein [42] recently observed the $6d^1 \rightarrow 5f^1$ fluorescence in Pa^{4+}/Cs_2ZrCl_6 at 4.2K. Transitions from the lowest $6d^1\Gamma_{8g}$ level to all levels of the $5f^1$ configuration were observed. In addition to the zero phonon lines, vibronic structure due to even parity vibrations of the $PaCl_6^{2-}$ anion were obtained. Analysis of this vibronic structure indicated that the $PaCl_6^{2-}$ bond is ~ 0.1 Å longer in the 6d excited configuration and that the Jahn-Teller distortion energies for the $6d\Gamma_{8g}$

quartet are quite small; $E_{dis}(e_g) \sim 28$ cm^{-1}, and $E_{dis}(t_{2g}) \sim 41$ cm^{-1}. One of the fluorescent transitions observed was extremely weak; calculations of the relative intensiites of the allowed electric dipole $6d\Gamma_{8g} \rightarrow 5f^1$ levels agreed quite well with the experimental relative intensities.

For the Th^{3+} free ion, the $5f^1$ configuration is situated about 10,000 cm^{-1} lower in energy than the $6d^1$ configuration. However for the Pa^{4+} ion in crystals, there is about a 25,000 cm^{-1} energy decrease between the centers of gravity of the two configurations compared to the free ion as noted earlier. Thus for Th^{3+} ions in solids, the $6d^1$ configuration may be lowest in energy. EPR investigations of the only crystallographically characterized Th^{3+} compound [4] confirm that for this compound, the $6d^1$ configuration is lowest in energy [43]. Calculations by Bursten, et al. [44] suggest that for other Th^{3+} compounds with different symmetry at the metal ion, the $6d^1$ orbitals may be significantly shifted to higher energy with the net result that the $5f^1$ configuration may again become the ground configuration.

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