OPTICAL STUDIES OF LANTHANIDE AND ACTINIDE IONS IN CALCIUM FLUORIDE

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ABSTRACT

Optical absorption and thermoluminescence measurements were used to study the effects of γ -irradiation on trivalent actinide ions in CaF_2 . Thermoluminescent glow curves for Np, Pu, Am and Cm (and, for comparison, the lanthanides Er, Ho and Tm) were measured between 100° and 300°K. These were found to be remarkably similar, with glow peaks occurring at nearly the same temperatures for each of the ions. The activation energies for each of the glow peaks were estimated. High resolution measurements of the spectra of the thermoluminescence showed that the emission is identical to the fluorescence of the trivalent ions, and determines the site symmetry of the emitting ion. Evidence was presented that the glow emission below 300°K originates from trivalent actinide ions in cubic sites. In the model proposed to explain these data, irradiation at 77°K produces hole traps and electrons which are localized near cubic Ac^{3+} ions. Heating allows a hole to diffuse to the site of a localized electron. The hole and extra electron recombine, leaving an excited trivalent actinide ion. Decay of this ion to its ground state results in the observed thermoluminescence.

When the $\text{Ac}^{3+}\text{-CaF}_2$ crystals were irradiated at 300°K , the actinide ion was oxidized to the tetravalent state. In the model proposed, heating allows electrons which had become trapped in the lattice to recombine with the Ac^{4+} ions. The decay of the newly formed Ac^{3+} ion to its ground state results in the observed thermoluminescence.

The optical Zeeman rotation spectra were taken of some selected transitions in Am^{3+} , Cm^{3+} and Nd^{3+} embedded in CaF_2 . Only symmetry sites arising from tetragonal compensation could be positively identified, although there was evidence for the existence of lower symmetries. This technique is of general applicability to problems of non-equivalent sites and provides a more positive identification than Zeeman studies restricted to a few crystallographic directions.

I. INTRODUCTION

Probably no other mineral shows such an abundance of colors and such brilliant luminescence as the fluorites (CaF_2); in fact, the word "fluorescence" was suggested by Stokes¹ because of the brilliant blue luminescence from many English fluorites. These minerals became the subject of numerous early investigations.² Microanalysis and improved crystal growing techniques showed that the phenomena occurring in the fluorites could be explained by the presence of trace amounts of foreign materials, in particular the rare earths.

The lanthanides and actinides (henceforth referred to collectively as "rare earths") are characterized by the progressive filling of the 4f- and 5f- shells, respectively, of their electronic configurations. The electrons contained in these shells are shielded by outer electrons from any strong interaction with their environment. The free ion electronic levels are usually studied by electrical discharges. This gives rise to a very complicated spectrum because (1) usually the ion is observed in several valence states simultaneously, and (2) the observed spectral lines are broadened by the high current requirements. On the other hand, if the ion is incorporated into a crystal it is held fixed and often present in only one oxidation state (usually 3+). Calcium fluoride is an ideal host material for the rare earths. It is hard and sturdy (this is particularly important for the radioactive actinides), takes to optical finishes, is transparent throughout a wide spectral range (1250 $\text{\AA}$ - 9 μ) and, most important, incorporates small amounts of rare earths isomorphically. Furthermore, it is a very good laser

host and indeed several lasers have been constructed from rare earths incorporated into calcium fluoride.³⁻⁸

Most of the work done on rare earths in calcium fluoride has been on the lanthanides. In this laboratory we have been extending these studies to include the actinides. Several difficulties arise: (1) Very often the amount of material available is prohibitively small. Experimental absorption intensities may be very weak. (2) The intrinsic radioactivity damages the crystal resulting in broad absorption bands which often obscure important spectral features, or mask them out completely. (3) The f-f transitions are in general broader than in the corresponding lanthanides. (4) Theoretical considerations are more complex because of greater j-j coupling.

In this dissertation a study is made of the γ -irradiation of actinide ions in CaF_2 . Effects quite different from those observed in the lanthanides are observed, in particular, the stabilization of the tetravalent state rather than the divalent state. The second section deals with the determination of local site symmetries using optical Zeeman spectroscopy.

II. BACKGROUND

A. Calcium Fluoride

The production of optical quality crystals of calcium fluoride⁹ has enabled it to become a popular host material for rare earth ions. Measurements of many of its properties with references to other works are given by Malitson¹⁰ and Balchelder and Simmons.¹¹ The CaF_2 lattice structure is face-centered cubic and belongs to the space group O_h^5 . The structure may be regarded as a regular cubic array of fluorine atoms with calcium ions at every other body-centered position. This is shown in Figure 1. The lattice constant is $5.45 \text{ \AA}$.¹²

B. Charge Compensation

When small amounts of rare earth ions are incorporated into CaF_2 , they replace the calcium ions; however, since they are most stable in the trivalent state, a valence mismatch occurs which must be compensated. A great deal of optical and magnetic resonance work has been done on these systems. Excellent summaries are given by Feofilov¹³ and by Weber and Bierig.¹⁴ The results of these studies show that several different charge compensation mechanisms may occur which depend upon the growth conditions, impurity concentrations and thermal treatments of the sample.¹⁵

The spectra of rare earth ions in CaF_2 can be classified into two groups. Crystals grown in an atmosphere containing oxygen produce a Type I spectra; crystals grown in an oxygen-free atmosphere produce a Type II spectra.¹⁶ This notation, however, can be confusing (see for example Reference 17) and perhaps is best avoided.

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Fig. 1. Crystal structure of CaF_2 .

In oxygen-free crystals, the most common trivalent rare earth site is one of tetragonal (C_{4v}) crystal-field symmetry. Charge compensation is attained by the presence of a F^- ion in one of the six nearest-neighbor interstitial sites at a distance $a/2 = 2.73 \text{ \AA}$. The crystal field symmetry axes are the $[100]$ crystallographic directions. This charge compensating mechanism has been well substantiated from density and lattice constant measurements,^{18,19} ionic conductivity experiments²⁰ and early paramagnetic resonance results,^{21,22} and is shown in Figure 2a. A crystal field of trigonal symmetry (C_{3v}) can arise if the fluoride ion enters into one of the eight second-nearest-neighbor interstitial positions²³ as shown in Figure 2b. The symmetry axes are the $[111]$ crystallographic directions. It is also possible for the charge-compensating interstitial fluoride ion to be located far from the rare earth ion, leaving it in a field which is essentially cubic. Since the interstitial fluoride ion is not tightly bound to the trivalent ion, at sufficiently high temperature it can diffuse through the lattice.²⁰ Friedman and Low²⁴ observed that crystals which were rapidly quenched from high temperatures favored cubic site formation. They argue that the fluoride ions are unable to diffuse to an energetically favorable site near the rare earth ion and are trapped elsewhere in the lattice.

If oxygen is allowed to enter the crystal several new means of charge compensation are possible. The most common mechanism gives rise to a new trigonal (C_{3v}) symmetry about the rare earth ion,^{16,25-27} It is believed that O^{2-} ions replace lattice fluorides at one of the eight cube corners surrounding the rare earth, resulting in an asymmetry

Fig. 2a. Charge compensation in CaF_2 . Compensation by nearest-neighbor interstitial fluoride.

Fig. 2b. Compensation by second nearest-neighbor interstitial fluoride.

about the body diagonal of the cube (See Figure 2c). Lower symmetries involving pairs, triads and higher order clusters of rare earth ions have been suggested by Amster and Wiggins.²⁸

Charge compensation may also be attained by the addition of small amounts of positive compensators, Me^+ ($Me^+ = Na^+, K^+, \text{ and } Ag^+$).²⁹ The resulting symmetry is usually orthorhombic (C_{2v}) and results from the replacement of two neighboring Ca^{2+} ions with a RE^{3+} ($RE = \text{rare earth}$) ion and a Me^+ ion.

C. Site Symmetry Determination

It is thus well established that when a trivalent rare earth ion is incorporated into CaF_2 several kinds of sites are created as a consequence of the various modes of compensation of the excess positive charge. The resultant sharp line optical spectra are very complex due to the superposition of spectra belonging to specific sites. Analysis of such a spectrum consists in grouping together lines which belong to a specific site and determining its symmetry. Several methods of analysis have appeared in the literature and are discussed below.

1. Concentration Series Method

The concentration series method³⁰ is based on an approximate thermodynamic calculation of the equilibria of site symmetries in $CaF_2 - RE^{3+}$ crystals by Osiko.³¹ Formulas were obtained relating the concentrations of RE^{3+} sites having different structure to the total concentration of rare earth impurity and to the equilibrium temperature. The calculation showed that there is a very characteristic dependence of

Fig. 2c. Compensation by substitutional O^{2-} .

the concentrations of different sites on the total concentration of RE^{3+} . At low concentrations the majority of ions should be in cubic sites. At higher concentrations the fraction of tetragonal centers should increase, and, at still higher concentrations, there should be a considerable fraction of orthorhombic centers. Preliminary investigations by Voronko and workers³⁰ showed that spectral lines can indeed be classified into distinct groups by their concentration dependence, but there is no unambiguous correlation with the theoretical calculations.

2. Correlation of Optical and EPR Data

The determination of site symmetries in $\text{RE}^{3+}\text{-CaF}_2$ by electron paramagnetic resonance is accomplished by examining a plot of lines (which corresponds to splitting values) as a function of angle of rotation about a known direction of the crystal (usually $[110]$) which is perpendicular to the dc and microwave fields. By making a careful comparison of optical and EPR data of several crystals grown under different conditions and having different concentrations, it should be possible to assign site symmetries from EPR data to optical lines. This method was first applied to gadolinium. Makovsky³² studied the absorption and emission spectra of $\text{Gd}^{3+}\text{-CaF}_2$ and established the crystal-line energy level schemes of Gd^{3+} in eight different sites. Later this work was extended to include SrF_2 and BaF_2 .³³ At about the same time Gilfanov et al.,³⁴⁻³⁶ working independently, carried out a similar series of experiments which confirm Makovsky's data. It was pointed out, however, that the correlation is not always straightforward.³⁴ The probability of a transition in EPR is almost independent of the symmetry of

the crystalline electric field; however, the probability of transitions between electronic levels responsible for the optical spectra can be very strongly dependent on the type of surroundings. For example, in the presence of a center of inversion (e.g., cubic symmetry) electric dipole-dipole transitions between levels within the same electronic configuration are forbidden, whereas in the absence of a center of inversion (e.g., tetragonal, trigonal) electric dipole-dipole transitions are allowed.³⁷ A similar analysis was carried out by Kirton and McLaughlin³⁸ on $\text{Yb}^{3+}\text{-CaF}_2$. Ten different sites were found; a correlation between EPR and optical spectra was found for six of these sites.

3. Piezospectroscopic Determination

The piezospectroscopic determination of local site symmetries in CaF_2 is based on the uniaxial elastic compression (or elongation) of the crystal. This anisotropic influence will have a different effect on sites oriented along different crystallographic axes. The theoretical aspects were worked out by Kaplyanskii³⁹ and recently have been extended by Malkin and co-workers.⁴¹ The technique has been applied to Eu^{3+} ,^{40,42,43} Sm^{3+} ,⁴⁰ Ho^{3+} ,⁴⁶ Ce^{3+} ,⁴⁶ and some divalent lanthanides.^{44,45}

4. Optical Zeeman Effect

The study of the Zeeman splitting of lines in RE-CaF_2 crystal spectra is becoming an increasingly popular tool. Very high magnetic fields are now available in superconducting magnets and pulsed magnets. A theoretical discussion of the Zeeman effect will be postponed until Section V A-3. We shall present here a survey of the literature.

The Zeeman effect in the optical spectra of $RE^{3+}-CaF_2$ crystals was first observed by Arkhangelskaya and Feofilov⁴⁷ and was used to determine the position of the O^{2-} compensator in the CaF_2 unit cell. At first Zeeman studies were mostly confined to the relatively simple case of cubic symmetry: Sm ,⁴⁸ Tm ,⁴⁹ and Eu ⁵⁰⁻⁵⁴ were studied in the divalent state; Yb ⁵⁵ and Eu ⁵⁶⁻⁵⁸ were studied in the trivalent state. The existence of non-cubic sites has been established by other investigators. Tetragonal charge compensation was found by Crozier⁵⁹ in $Ce^{3+}-CaF_2$ and independently by Russian workers.^{60,61} Masui and Ibuki⁶² used a pulsed magnetic field up to 130 kG. to study two intense trigonal lines, probably due to O^{2-} compensation, in $Pr^{3+}-CaF_2$. Kirton and White⁵⁵ used the Zeeman effect to confirm the cubic, tetragonal and trigonal sites reported by Kirton and McLaughlin³⁸ who correlated EPR and optical spectra. In what has probably been the most complete analysis to date, Rector, Pandey and Moos⁶³ found tetragonal sites in $Er^{3+}-CaF_2$ by study of the Zeeman pattern of the lines as a function of rotation about the $[110]$ axis of the crystal. This technique is of general applicability and provides considerably more information than Zeeman studies restricted to a few crystallographic directions.

5. Other Methods

Several other methods have been used to determine the site symmetries in $RE-CaF_2$ single crystals. Rabbiner assumed a pure cubic^{64,65} or pure tetragonal⁶⁶ symmetry in his crystals and calculated the theoretical crystal field energy level schemes to first order of perturbation theory. The agreement between observed and calculated lines confirmed the proposed symmetry. A similar calculation was carried out by Zverev and Smirov⁶⁷ for trigonal (O^{2-} compensation) Eu^{3+} sites in CaF_2 .

Using a technique developed by Feofilov⁶⁸, Ewanizky and co-workers⁶⁹ measured the polarizarization of fluorescence from $\text{Sm}^{3+}\text{-CaF}_2$ crystals. They concluded that tetragonal and trigonal symmetries were involved.

It has been reported that fluorescence from strictly cubic sites can be induced in $\text{RE}^{3+}\text{-CaF}_2$ by excitation with x-rays⁷⁰ or γ -rays.⁷¹ The mechanism is based on the formation of divalent ions in CaF_2 which will be discussed in the next section.

Finally, several methods have been introduced which cannot be used to determine the nature and crystallographic location of the charge compensator but can help group together spectral lines which arise from the same mechanism. Makovsky⁷² was able to group spectral lines with the same afterglow characteristics; Luks, *et al.*⁷³ grouped lines with the same luminescence quenching time. Voronko and co-workers⁷⁴ developed a technique which selectively excited the luminescence from individual site symmetries.

D. Effects of γ -Irradiation

1. Valence Changes

Much research has been done on the reduction of lanthanide ions in calcium fluoride to the divalent state. These ions have broad $4f^n \rightarrow 4f^{n-1}d$ absorptions in the visible spectral region where strong pumps are available and thus are useful in lasers. In general the reduction techniques are the same as those used to produce color centers in alkali halides and alkaline earth fluorides (see Section II-D3).

A few of the lanthanide ions are relatively stable in the divalent state and significant concentrations can be grown in the crystal under reducing conditions. Sm^{2+} , Eu^{2+} and Yb^{2+} were studied by Feofilov⁷⁵ in 1956. For Eu^{2+} and Yb^{2+} the stability can be attributed to the half-filled (f^7) and completely filled (f^{14}) electronic configurations.

All of the lanthanides in calcium fluoride can be chemically reduced by heating the crystal for several hours at 750-950°C in an atmosphere of calcium vapor.⁷⁶ The conversion is close to 100%. Solid-state electrolysis gives a similar result.⁷⁷⁻⁷⁹

Divalent lanthanides can also be produced by exposure to high energy electrons,⁸⁰ x-rays⁸¹⁻⁸³ and γ -rays.⁸⁴ The conversion efficiency is not high and is strongly dependent upon the particular sample: Sabisky⁸⁵ obtained a maximum conversion of 17%; O'Connor and Bostick⁸⁰ in some crystals had a 50% conversion; Galaktionova *et al.*⁸⁶ managed only 5% conversion. Furthermore the reduction is unstable with respect to ultra-violet and visible light⁸⁷ and heat (see the following section).

There is evidence that only those lanthanide ions with non-local compensators (cubic sites) can be reduced to the divalent state. Hayes and Twidell⁸² irradiated samples containing Tm^{3+} at 77°K and found divalent Tm only at cubic sites. They suggest that only those ions initially at cubic sites are reduced since it is unlikely that the charge-compensating ion is mobile at 77°K. Low and Ranon⁸⁸ produced Tm^{2+} in cubic sites by γ -irradiation at 300°K but feel that the compensator may be mobile at that temperature. Further evidence of Tm^{2+} at cubic sites is given by

Hayes and Twidell⁸⁹ and by Anderson and co-workers.⁹⁰ Several authors^{85,89,91,92} report the presence of Ho^{2+} in cubic sites after irradiation. Sabisky⁸⁵ did a quantitative study of Ho^{2+} production. The conversion efficiency was low for relatively large or small Ho^{3+} concentrations. For large concentrations of Ho^{3+} , cluster formation may reduce the relative number of $3+$ ions in cubic sites; for low concentrations, minute amounts of oxygen may act as local compensators.⁸⁷

In this laboratory we have been involved in studying the effects of γ -irradiation on actinide elements embedded in calcium fluoride. Edelstein and co-workers⁹³ showed that divalent Am can be formed in CaF_2 by γ -irradiation of the $3+$ ion. The mechanism seems to be completely analogous to the lanthanides. Recently, however, McLaughlin *et al.*⁹⁴ reported that in Pu-CaF_2 the ion is initially presented in the trivalent state but, due to the intense α -decay of the Pu nucleus, some of the Pu is converted to the tetravalent state. This effect could be duplicated by the irradiation from a ⁶⁰Co source. This stabilization of the tetravalent state in the CaF_2 matrix is a surprising effect, since it increases rather than destroys the local charge imbalance. The mechanism is not understood and this dissertation will be concerned in part with similar systems.

2. Thermoluminescence

If trivalent lanthanide ions (Ln^{3+}) in CaF_2 which have been irradiated are then heated above the irradiation temperature, they emit light. This phenomenon is known as afterglow or, more commonly thermoluminescence. Merz and Pershan⁹⁵ γ -irradiated all of the available

lanthanides at 77°K, and subsequently warmed the crystals to above room temperature. The glow intensity was integrated over wavelength and plotted as a function of sample temperature. The most striking result is that the temperatures of thermoluminescent emission maxima are essentially independent of the lanthanide. The relative intensities differ from one lanthanide to another, and in some cases are weak or missing, but in general the peaks occur at nearly the same temperatures. This suggests that the emission cannot be associated with direct thermal ionization of the divalent ion which would be a function of the ionization potential of each lanthanide, modified by the crystalline environment, but must be associated with the lattice. Similar results were reported by Arkhangelskaya⁹⁶ for Er, Ho, Tm and Dy.

The situation is not so clear for the high temperature glow peaks (those occurring above room temperature), where the peak temperatures are no longer coincident. Fong⁸⁵ has suggested that this process involves the transfer of electrons into the valence band and hence is dependent upon the particular lanthanide. More recently it has been suggested that the process involves the excitation of an f electron to the d bands.⁹⁷

Although the thermoluminescent glow peaks do not depend strongly on the particular lanthanide, the emission spectra are unique and correspond to the fluorescence of the trivalent ion. There is evidence that for peaks occurring below room temperature, the emission corresponds to the trivalent ion in cubic symmetry.^{84,95} The high temperature peaks correspond to emission from the trivalent ion in tetragonal symmetry. Merz and Pershan⁸⁵ proposed the following simple model:

The lanthanide ions converted to the divalent state are initially in cubic sites. The electrons come from compensators located far away or from non-local lattice fluoride ions. Electron holes (electron deficient centers) are left behind. As the temperature is increased, the holes migrate to the Ln^{2+} and capture its extra electron leaving the now trivalent ion in an excited state. This ion then decays to its ground state giving rise to the observed emission. For the low temperature peaks this hole center must leave the Ln^{3+} in a cubic site. Such centers may exist in a number of configurations and are discussed in a recent review by Beaumont et al.⁹⁸ The high temperature peaks may be explained by the diffusion of interstitial fluorine atoms which had been far from the ion. When they approach the divalent ion, they provided the tetragonal symmetry during the electron recombination process.

There are, however, some conflicting results which have appeared in the literature. It is apparent that the amounts of impurities and growth conditions may have a great effect on the thermoluminescence glow and the emission spectrum. Makovsky⁷² and Schlesinger and Whippey,⁹⁹ working independently, studied the low temperature thermoluminescence of $\text{Gd}^{3+}\text{-CaF}_2$ and concluded that it consists of the superposition of emission spectra from several site symmetries. Schlesinger and Whippey¹⁰⁰ later studied $\text{Ce}^{3+}\text{-CaF}_2$ and concluded that the low temperature thermoluminescence is due to the trivalent ion in sites of at least two kinds of symmetry, one of which is trigonal.

The thermoluminescence of actinide ions in CaF_2 has not been studied in detail. Edelstein and co-workers⁹³ reported that the

radiation damage in crystals of $\text{Am}^{3+}\text{-CaF}_2$ can be removed by heating the crystal to about 500°C for one hour. This is accompanied by the green glow characteristic of Am^{3+} ions. McLaughlin *et al.*⁹⁴ were able to obtain crude thermoluminescence measurements on radiation damaged Pu-CaF_2 and assumed it to be characteristic of the $3+$ ion. The thermoluminescence of Pu-CaF_2 would not be expected to follow exactly the model proposed by Merz and Pershan; the formation of the tetravalent state would be accompanied by the formation of electron traps rather than electron holes. The characterization of this type of thermoluminescence is one of the major concerns of this dissertation.

3. Color Centers

It is apparent from the recent literature on color centers in alkaline earth fluorides that the significance of the broad absorption bands is still controversial. The spectra are often confusing, impurity-dependent^{101,102} and variable;¹⁰³ consequently, the characterization of these centers in terms of the well-known alkali halide centers, such as F, R, M, N, O, H and V, has been largely unsuccessful. The anomalous colorization behavior of CaF_2 , in part at least, is from the particular nature of the fluorite structure in which the spacious interstitial sites may readily accommodate fluoride ions.¹⁰⁴ The effect of the fluorite structure upon the incorporation of impurities is evidenced by the "intrinsic" presence of yttrium¹⁰⁵ and the large solvability of RE^{3+} ions in CaF_2 . Furthermore, oxygen¹⁰⁶ and hydrogen¹⁰⁷ impurities undoubtedly play a large role in the optical properties of the crystal.

Recently, however, an analogy has been drawn between the band at 3750 Å in CaF_2 and the well-known F-center (an electron trapped at an anionic vacancy) of the alkali halides. Mollwo¹⁰⁸ and more recently Arends¹⁰⁹ were able to produce this band in additively colored crystals. Ratman¹¹⁰ produced the band by irradiating at temperatures between 180° and 250° C. Kamikawa and co-workers¹¹¹ found that the F-center can also be formed by irradiating at 4.2° K.

Another center recently identified in calcium fluoride is the V_k center, or self-trapped hole.¹¹² The center is basically a form of the F_2^- molecule. Its formation is enhanced by the presence of trivalent lanthanides, and may correspond to the band at 3100° Å which occurs in irradiated Ln^{3+} - CaF_2 crystals.¹¹³

The overall situation in CaF_2 seems to be that it is relatively hard to produce color centers in the pure material, especially by irradiation; however, the presence of impurities enhances the formation of these centers, especially if the impurity has a different valence state than the ion it replaces, such as Ln^{3+} replacing Ca^{2+} . This center acts as an electron trap and the most likely centers that will be formed during irradiation are those that can supply electrons to the lanthanides. This would result in the formation of trapped holes rather than F-centers or other trapped electron centers. However, trapped electron centers would be expected in CaF_2 crystals containing Pu^{3+} which actually acts as an electron hole, since it can be oxidized to the tetravalent state.

III. EXPERIMENTAL PROCEDURES

A. Sample Preparation

The majority of the samples used for the experiments reported in this dissertation were grown by the author or Dr. Norman Edelstein using the Bridgman-Stockbarger technique. In this method, powdered CaF_2 and part of an oriented seed crystal are melted in a graphite crucible and then slowly lowered through a sharp temperature gradient. This type of crystal furnace has been fully described¹¹⁴⁻¹¹⁶ and will not be discussed further here. Other samples containing fixed amounts of lanthanides or uranium were obtained from Optovac, Inc.¹¹⁷

The CaF_2 used to grow these crystals was obtained in crystal form from Optovac, Inc., and was crushed before being placed in the crucibles. Approximately 2 wt.% PbF_2 was also added as a scavenger to remove water and oxygen from the crystal.¹¹⁴ Cylindrical seed crystals, 4 mm or 3/16" in diameter, and oriented along the [111], [110] or [100] crystallographic directions were also obtained from Optovac, Inc.

The concentration of dopant ion was determined only by the amount of rare earth added to the charge. This varied from 0.01-0.8 wt.%; however, this is known to be inaccurate and only gives an order of magnitude estimate. The lanthanide ions were added dry as the trifluorides; the actinide ions were pipetted from concentrated acidic solutions.

B. Spectral Measurements

1. Low Resolution

Spectral measurements were made photographically at low resolution using a Jarrell-Ash F/6.3 plane grating spectrograph. Three gratings were used with 300, 600 and 1200 grooves/mm. The 1200 grooves/mm grating had, in the first order, a reciprocal linear dispersion of approximately 10 Å/mm. at the blaze (5000 Å). The entrance slit was usually 20-100 μ . Kodak spectroscopic plates Type 103a-F and Type IV-F were used for most of the exposures in the visible; Type I-N and Type I-Z were used in the infrared. The I-Z plates were hypersensitized¹¹⁸ by bathing the plate for three minutes in a dilute ammonia solution (4 parts of 28% NH_3 diluted with 100 parts of H_2O) at a temperature of about 40°F. Following this treatment the plate was bathed for three minutes in CH_3OH and then rapidly dried in a stream of air from a blower.

A Cary Model 14 recording spectrometer was used in infrared regions where photographic plates are not sensitive and in the complete 3000 Å - 2.6 μ region for general spectral surveys. Samples were carefully masked to insure that all detected radiation passed through the sample rather than around it, since the dimensions of the light beam in the sample compartment were often several times larger than those of the crystal. Usually the reference beam also had to be masked to compensate for the low light intensity in the sample compartment.

Quantitative absorption measurements were made with a Jarrell-Ash Model 82-000 0.5 meter Ebert scanning spectrometer, used in conjunction

with an RCA 7102 photomultiplier. The monochrometer was equipped with a 295 grooves/mm grating giving in the first order a reciprocal linear dispersion of about $64 \text{ \AA/mm}$ at the exit slit. The slit width was usually 100μ . The RCA 7102 photomultiplier has an S-1 response, which in the IR peaks at $8000 \text{ \AA}$ and has 50% sensitivity at approximately $6000 \text{ \AA}$ and $9600 \text{ \AA}$. The anode supply voltage was varied between 800 and 1000 volts depending on the light intensity. The photomultiplier was encased in a PM-101 Coolable Photomultiplier Assembly (Electro Optics Associates) and was cooled by a flow of cold nitrogen gas.

2. High Resolution

High resolution measurements in the Zeeman studies were made photographically using a 3.4 meter Jarrell-Ash plane grating spectrograph, Model 7102. A 300 grooves/mm grating with a peak intensity at approximately 59° , or $57,000 \text{ \AA}$, was used in the 6-13 order range. The order of interest was isolated by means of filters. A thorium electrodeless discharge lamp was used for the reference spectrum.

IV. γ -IRRADIATION OF ACTINIDE IONS IN CaF_2

A. Sharp Line Spectra

1. Neptunium

The isotope ^{237}Np is an alpha emitter with a half-life of 2.2×10^6 years. It is a by-product in the operation of nuclear reactors and hence is formed in large amounts. Until recently neptunium had only intrinsic interest as a new element with unique chemical properties.¹¹⁹ However, ^{237}Np may soon become valuable since it is the source for the short-lived ^{238}Pu , which is being used as an isotopic power source. Moreover, the optical properties of Np in single crystals have become of interest because of the suitability of Np^{4+} ions for laser applications.¹²⁰

a. Np^{3+} characterization Neptunium is known to exist in a number of oxidation states. The trivalent ion is stable in solution in the absence of oxygen, but rapidly oxidizes to Np^{4+} in the presence of air. The stable form of pentavalent Np in aqueous solution is NpO_2^+ ; it disproportionates in the presence of fluoride ion or concentrated acid. The NpO_2^+ ion is similar to the uranyl ion; Np(VI) can also exist in nonoxygenated form as the volatile NpF_6 . Recently the heptavalent state of Np has been reported.¹²¹

When lanthanide ions are incorporated into CaF_2 the trivalent state is usually stabilized. This however would not necessarily be true for Np, which is not like the lanthanides in that it can exist in several oxidation states. For example Phillips and Feldman¹²⁰ incorporated Np into single crystals of PbWO_4 and found that Np enters the crystal

predominately in the tetravalent state, occupying Pb^{2+} lattice sites. Another oxidation state, probably Np^{6+} , also appears but can be eliminated by the presence of Na^+ in the crystal.

Single crystals of CaF_2 doped with 0.1-0.2 wt. % of ^{237}Np were grown in this laboratory. The crystals were light green or colorless and showed no darkening due to self-irradiation damage over a period of several months. In Figure 3 the absorption spectrum of $\text{Np}-\text{CaF}_2$ is compared with Krupke and Gruber's data of Np^{3+} in LaBr_3 .¹²² Further comparison with Waggener's solution data of several oxidation states of neptunium¹²³ indicates that the main oxidation state present is $3+$ and that Np^{4+} and Np^{6+} are not present in any significant amount. The presence of Np^{5+} cannot be rigorously excluded since its only intense absorption peak overlaps with an intense Np^{3+} peak; however, since crystals were not grown in an oxidizing atmosphere (and indeed since the graphite crucible itself acts as a reducing agent) and since the $4+$ oxidation state, which is known to be stable in solution, did not form in the crystal, it seems unlikely that a higher oxidation state could be present. Krupke's absorption data in LaBr_3 consists of clearly defined groups of sharp lines whereas in CaF_2 the spectrum is considerably more complex. This is due to (1) a larger crystal field splitting in CaF_2 , and (2) the existence of different site symmetries in the charge-compensated CaF_2 .

b. Np^{4+} formation When the $\text{Np}^{3+}-\text{CaF}_2$ crystal was irradiated for 15 hours at 0°C or at room temperature in a ^{60}Co source, it turned from its original light green color to a deep blue-green. An intense

Fig. 3. Comparison of Np spectra in various media.

broad absorption appeared through the visible region (which will be discussed in Section IV-B) and three new groups of sharp lines appeared. In Figure III it is shown that these three groups agree extremely well with the most intense Np^{4+} absorptions reported by Waggener in D_2O . It was not possible to observe the Np^{4+} absorption in $\sim 1.2\mu$ because the $3+$ absorption is so intense in that region. Table 1 lists the $\text{Np}^{4+}\text{-CaF}_2$ wavelengths and their corresponding J values, calculated by Conway.¹²⁴ These assignments are in agreement with the recent work of Varga et al.¹²⁵ on NpF_4 and Gruber and Menzel^{126,127} on $\text{Np}^{4+}\text{-ThO}_2$. The assignment of $\sim 7000 \text{ \AA}$ group is not straightforward because of the superposition of four J levels in that region.

An attempt was made to better characterize Np^{4+} by growing a CaF_2 crystal which contains only tetravalent Np. Recently in this laboratory McLaughlin and co-workers¹²⁸ were able to grow a U-CaF_2 crystal containing only the tetravalent state by using a small carbon resistance furnace. The starting material consisted of crystalline CaF_2 , 2 wt. % PbF_2 and 1 wt. % UF_4 and was held in the molten state for only a few seconds. A similar experiment using Np was carried out using the same apparatus; however, an extremely complex spectrum resulted suggesting the presence of at least two Np oxidation states.

The γ -irradiation induced Np^{4+} is not completely stable and decreases slightly in intensity over a period of a few months at room temperature. The broad absorption band can be bleached out and the Np^{4+} structure completely destroyed by heating the crystal to $\sim 400^\circ\text{C}$. The

Table 1. Mg^{4+} - CaF_2 absorption lines.

Wavelength (Å)	Wavenumber (cm^{-1})	J Value
7257	13777	
7282	13728	
7313	13671	15/2, 3/2, 5/2, 3/2
7328	13643	
7333	13633	
7347	13608	
9672	10336	
9694	10313	
9816	10185	13/2
9870	10128	
9951	10046	
16630	6010	
16750	5967	
16810	5948	
16950	5897	
16870	5890	11/2
17010	5876	
17040	5868	
17290	5780	

crystal can also be bleached by ultraviolet light. A one hour exposure with 3000-9000 Å light from a 1000 watt Hg lamp reduced the intensity of the broad absorption by more than 50%. Additional exposures seemed to have little effect.

c. A quantitative study A high resolution quantitative study was made of the growth of Np^{4+} and the decay of Np^{3+} spectral lines upon γ -irradiation at 0°C. Accurate measurements were not possible above 1 μ because detection with PbS is not nearly as sensitive as with a photomultiplier. Quantitative studies in the visible were also impractical because of the intense broad absorption which appears when the crystal is irradiated. Consequently the only spectral region that could be studied was 9400-10,000 Å. The absorption spectrum of Np-CaF_2 before and after irradiation is shown in Figure 4. Of 12 Np^{3+} lines which could be followed, eight remained unchanged and four decreased to 1/3 of their original intensity. In addition, four new sharp lines grew in, which were previously assigned to Np^{4+} . The growth and decay of these lines as a function of irradiation time is shown in Figure 5. The height of the absorption band is assumed to be proportional to the number of ions present, since the shape of these lines does not depend on the concentration.

Let us denote the optical densities of Np^{3+} and Np^{4+} by D_1 and D_2 respectively. The data of Figure 5 are found over most of the range to satisfy the relation 129, 130

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Fig. 4. Absorption spectra of $\text{Np}^{3+}\text{-CaF}_2$: a) before irradiation, b) 10 hrs irradiation at 0°C . The arrows indicate the absorption lines which increase or decrease upon irradiation.

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Fig. 5. Growth and decay of absorption lines in $Np-CaF_2$ as a function of irradiation time.

$$\frac{D_{1,0} - D_1}{D_{1,0} - D_{1,\infty}} = \frac{D_{2,0} - D_2}{D_{2,0} - D_{2,\infty}} \quad (1)$$

where the additional subscripts 0 and ∞ represent, respectively, the optical densities of the initial (unirradiated) state and the state irradiated to saturation. In other words the relative weakening of the Np^{3+} bands is equal to the relative growth of the Np^{4+} bands and the processes proceed in parallel. The data for four pairs of Np^{3+} , Np^{4+} bands are plotted in Figure 6. The slope of the line is nearly one. Equation (1) is satisfied, and there does indeed exist a 1:1 correspondence. Furthermore the Np^{3+} lines which do decrease in intensity upon irradiation at 0°C , decrease at the same rate.

In the above argument it was tacitly assumed that the new lines at $\sim 9500 \text{ \AA}$ are due to Np^{4+} because they appear under the same conditions as the Np^{4+} lines at $\sim 1.7\mu$. This latter group of lines is actually the only definitive $4+$ structure since no absorption lines from other Np oxidation states appear in this region. There exists of course the possibility that the new lines at $\sim 9500 \text{ \AA}$ are not due to Np^{4+} but are associated with another irradiation effect, namely the conversion of Np^{3+} ions from one site to another. Similar processes have been reported in literature^{58, 131-134} for the lanthanides. In the present investigation however this possibility must be excluded since no new lines appear upon γ -irradiation at 0°C in the Np^{3+} structure at $\sim 2.3 \mu$.

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Fig. 6. Plot of relative rate of growth of Np^{4+} absorption lines versus relative rate of decay of Np^{3+} absorption lines.

From the arguments of the preceding paragraphs, the effect of γ -irradiation on $\text{Np}^{3+}\text{-CaF}_2$ may be represented by the process:

If the symbol " γ " denotes the assumption that an electron is separated from Np^{3+} by a direct ionization process, then the rate of decay of Np^{3+} is given by:

$$-\frac{dn_1}{dt} = kn_1 \quad (3)$$

where n_1 is the concentration of Np^{3+} ions which can undergo oxidation. Equation (1) which was previously confirmed can be written in a slightly different form as:

$$-\frac{dn_1}{dt} = \frac{dn_2}{dt} \quad (4)$$

where n_2 is the concentration of Np^{4+} ions. Equations (3) and (4) integrate to the familiar exponential rate equations:

$$n_1 = n_0 e^{-kt}, \quad n_2 = n_0 (1 - e^{-kt}) \quad (5)$$

where n_0 denotes the initial concentration of Np^{3+} ions which can undergo oxidation. Analysis of the data in Figure 5, however, shows that the Np^{3+} decay rate and Np^{4+} growth rate do not follow first order kinetics,

but are of some higher order. Therefore it must be inferred that the "γ" in Equation (2) does not denote a simple ionization process but rather implies a more complex mechanism, the net result of which is Equation (2).

Complete wavelength measurements of $\text{Np}^{4+}\text{-CaF}_2$ could only be made on the 1.7μ group because the other groups are masked by strong Np^{3+} absorptions. The transition in Russell-Saunders coupling is $^4I_{9/2} \rightarrow ^4I_{11/2}$ but is perhaps better regarded simply as a $J = 9/2 \rightarrow J = 11/2$ transition. Since $\text{Np}^{4+} (f^3)$ has an odd number of electrons, Kramer's degeneracy is present, and in the absence of an external magnetic field the maximum number of energy levels that can exist is five and six for $J = 9/2$ and $J = 11/2$, respectively.³⁷ If it is assumed that at 77°K only the ground state is populated, then, since eight spectral lines were assigned to Np^{4+} , there must be at least two different site symmetries present. If, however, excited levels in the ground state configuration are significantly populated at 77°K, then the eight observed lines could possibly be assigned to a single site symmetry. Spectral measurements in this region are precise to $\pm 1.5 \text{ Å} (\pm 0.5 \text{ cm}^{-1})$. Computation of all possible energy differences between the observed levels showed that no pair differences are the same to within experimental error ($\pm 1 \text{ cm}^{-1}$). The Np^{4+} must therefore be present in more than one site symmetry.

d. γ-irradiation at 77°K Irradiation of the $\text{Np}^{3+}\text{-CaF}_2$ crystal immersed in liquid nitrogen for 48 hours produces only two Np^{4+} lines in the 1.7 μ region (at 1.663 μ and 1.704 μ). Since these lines also grow

in at room temperature, the presence of at least two Np^{4+} sites at room temperature is confirmed. An approximate comparison of the efficiency of Np^{4+} production at 77°K and ~300°K can be made by assuming that the absorption coefficients of the different Np^{4+} lines are comparable. Integration of the total Np^{4+} absorptions at ~1.7 μ showed that the production is 15 times greater at the higher temperature. Even the production of what is probably a single site symmetry (that is, the lines at 1.663 μ and 1.704 μ) is greater at room temperature, though only by a factor of two. The Np^{4+} can be partially destroyed by heating the crystal to room temperature and completely destroyed by heating to ~400°C.

The most pronounced effect of the 77°K irradiation, however, is the appearance of three new intense absorptions in the infrared. Of the Np^{3+} lines between 1.9 and 2.4 μ which could be quantitatively studied, three new lines appeared, one line which was originally present increased in intensity significantly, two lines decreased in intensity and 20 lines were unchanged (Table 2). Warming the crystal to room temperature only partially regenerated the original spectrum; heating to ~400°C was necessary for complete restoration. These spectral changes are shown in Figure 7. It must be emphasized that the new Np^{3+} structure appears only in the low temperature irradiation. Thus the Np^{3+} formation at 77°K is not mechanistically related to the Np^{4+} formation since they have a different temperature dependence. The most obvious explanation is that γ -irradiation at 77°K produces a new Np^{3+} site:

Table 2. Spectral changes upon γ -irradiation of $\text{Np}^{3+}\text{-CaF}_2$ at 77°K.

New Absorption Lines (μ)	Lines Decreasing in Intensity (μ)	Lines Increasing in Intensity (μ)
1.944	2.331	2.196
2.079	2.337	
2.240

Fig. 7. Np-CaF₂ absorption spectra: a) crystal bleached, b) 48 hrs. γ -irradiation at 77°K, c) crystal bleached to room temperature.

Site b is unstable and the reaction may be thermally reversed.

e. Np^{3+} fluorescence The fluorescence of $\text{Np}^{3+}\text{-CaF}_2$ at 77°K , excited with 3000-5000 Å light from a 1000 watt Hg lamp, is shown in Figure 8. The absence of fluorescence in the visible may be attributed to the high concentration of J levels in that region which makes non-radiative de-excitation more probable.¹³⁵

2. Plutonium

The optical spectra of Pu in CaF_2 have been investigated by McLaughlin and co-workers⁹⁴ in this laboratory. Crystals grown with ^{239}Pu (half-life = 2.4×10^4 years) are light blue and gradually change to a deeper blue over the period of a few months. Crystals doped with ^{238}Pu (half-life = 86.4 years) darken in a few days. The plutonium is initially present in the $3+$ state and as a result of the α -decay of the Pu nucleus, new lines grow into the spectrum which were assigned to Pu^{4+} . The identification of the new oxidation state was not conclusive upon comparison with the spectrum of Pu^{4+} in 1M HClO_4 ¹³⁶ and required a further comparison with a mineral oil mull of Pu^{4+} coprecipitated with CaF_2 . In addition to the sharp lines several broad absorptions also grew in which will be discussed in Section IV-B. It was also reported that when the crystal was kept at 77°K after annealing, no new sharp lines grew in indicating that no Pu^{4+} is formed at this temperature.

In light of the neptunium results, these crystals were reexamined. Because of the broad absorptions throughout the visible, only

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Fig. 8. Fluorescence of Eu^{3+} - CaF_2 at 77°K .

the lines at 1.85μ could be used to monitor the Pu^{4+} concentration. A $^{239}\text{Pu}-\text{CaF}_2$ crystal containing 7.5 mg of Pu was irradiated for 48 hours at room temperature in a ^{60}Co source. Seven sharp lines characteristic of tetravalent plutonium appeared between 1.83 and 1.89μ . The crystal was bleached by heating to 400°C and then irradiated 48 hours at 77°K . Two sharp Pu^{4+} lines were observed at 1.836 and 1.843μ ; their intensities were approximately half of the corresponding lines in the room temperature irradiation.

Unfortunately a more detailed analysis of $\text{Pu}-\text{CaF}_2$ is not practical because the absorptions are not intense (approximately an order of magnitude less than the neptunium intensities, for comparable concentrations). Indeed the detection of the tetravalent state at 77°K was only possible in a very concentrated crystal and at very high radiation dosages.

3. Curium

The optical spectrum of Cm in CaF_2 has been investigated in this laboratory and preliminary results have been reported by Edelstein et al.¹³⁷ Calcium fluoride crystals doped with ^{244}Cm (half-life = 18 years) are initially colorless but rapidly become red and eventually turn black due to self-irradiation damage. A characteristic orange glow at $6000 \text{ \AA}$, due to the $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition of Cm^{3+} is always present. Initially only the $3+$ ion is present but sharp lines due to Cm^{4+} rapidly appear. In agreement with the Np and Pu results, fewer lines grow in when the irradiation occurs at 77°K . Unfortunately, a

very intense broad absorption also grows in which obscures the weak Ce^{3+} and Ce^{4+} absorptions and makes further analysis of the absorption spectrum unfeasible.

The intense fluorescence of $\text{Ce}^{3+}-\text{CaF}_2$ is very complex due to the superposition of several site symmetries and will be discussed in connection with the thermoluminescence of Ce in Section IVC-3c.

4. Uranium

The optical spectrum of uranium in CaF_2 has been reported by numerous investigators^{128, 138-148}; recently, however, conflicting results have appeared in the literature. Hargreaves¹⁴⁷ has grown green, red and yellow crystals of $\text{U}-\text{CaF}_2$ and argues that they represent uranium in the di-, tri- and tetravalent states, respectively. McLaughlin *et al.*¹²⁸, using chemical analysis, determined that Hargreaves "green" crystal contains U^{4+} and the "yellow" crystal contains U^{6+} .

The effects of γ -irradiation on red U^{3+} crystals have been studied in this laboratory. A very concentrated red crystal was found to be contaminated by "green" U spectral lines between 1.50 and 1.65 μ . Irradiation at room temperature for 64 hours increased the intensity of these lines approximately 50% which suggests the process:

or

depending on the assignment of the "green" U-CaF_2 .

5. Americium

Am-CaF_2 crystals were studied by Edelstein and co-workers⁹³ using optical and EPR techniques, Americium is incorporated into calcium fluoride as the trivalent ion and, like the lanthanides, is converted to the divalent state by γ -irradiation. The unusual stability of Am^{2+} may be attributed to the half-filled electron-shell configuration, f^7 .

B. Broad Absorption Spectra

When $\text{Ac}^{3+}\text{-CaF}_2$ (here, "Ac" is not meant to include Am, which shows anomalous behavior) crystals are γ -irradiated, two new spectral features appear: (1) groups of sharp lines, characteristic of the tetravalent state, and (2) intense broad absorptions. These latter spectral changes are shown in Figure 9. The most striking feature is that the broad absorption band maxima occur at approximately the same wavelength for all of the actinides, with the exception of americium. These wavelengths are listed in Table 3. The wavelength of the most intense curium absorption shifts toward the red as the radiation dosage is increased. All other absorptions, however, are independent of the dosage. Only one band was observed for $\text{U}^{3+}\text{-CaF}_2$ and its wavelength could only be estimated because it is superimposed upon intense U^{3+} absorptions. This band in U is considerably less intense than in the other actinides which might explain the absence of absorptions at $\sim 8000 \text{ \AA}$ and $\sim 1.05 \mu$. The same results are obtained when the crystals

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Fig. 9. Broad absorption spectra of $\text{Ac}^{3+}\text{-CaF}_2$ after 3 hrs. γ -irradiation. The dotted lines indicate the position of absorption maxima.

Table 3. Wavelengths of broad absorptions in $\text{Ac}^{3+}\text{-CaF}_2$.

U		5500 Å		
Np		5800 Å		1.05 μ
Pu	3800 Å sh	5800 Å	8100 Å	1.07 μ
		4800-		
Cm	3900 Å sh	5400 Å	7800 Å	1.06 μ

are irradiated at 77°K, except the absorptions are not as intense for comparable dosages. The Np, Pu, and Cm broad absorption intensities are reduced approximately by factors of 10, three, and two, respectively.

Since the positions of the absorption maxima are independent of the dopant ion, they are undoubtedly related to the defects of calcium fluoride itself, and therefore these broad absorptions are assigned to color centers. No report of this particular group of color centers appears in the literature (however, see Section IV D-3 for a discussion). Most of the defects in CaF_2 have been attributed to electron holes (electron deficient centers) which result when small amounts of trivalent lanthanide impurities take electrons from the lattice during the reduction process. In these crystals, however, the color centers are the result of electrons which are released by the Ac^{3+} ions, according to Equation (2), and are trapped in the lattice. This also explains the anomalous behavior of americium, which acts like a lanthanide rather than an actinide.

C. Thermoluminescence

Thermoluminescence has been a widely used method in the investigation of trapping levels in crystals, particularly the alkali halides.¹⁴⁹ Several glow peaks are obtained upon heating a crystal colored by γ -irradiation; these peaks are generally considered to arise from the release of carriers from different trapping levels. Early investigators showed that glow peaks appear at temperatures nearly proportional to their activation energies.^{150,151}

A detailed thermoluminescence model has been presented elsewhere,¹⁵²⁻¹⁵⁴ and the treatment here is meant to serve only as an introduction. For an ionic crystal the trapping levels may be described by the band model shown in Figure 10. A series of localized levels, N_i , may exist in the forbidden gap below the conduction band, and serve as electron traps. Similarly, M_j levels near the valence band are assumed to serve as hole traps. Ionizing radiation causes electrons to be trapped at the N_i trapping levels, and holes at the M_j levels. Thermoluminescence may then arise from one or more of the transitions involved in the process of recombination of a trapped electron with a trapped hole. Direct recombinations are very improbable, and hence traps are stable at low temperatures. Thermal release of carriers from one of the N_i or M_j levels is necessary for the thermoluminescence. The activation energy for the emission of a given glow peak is therefore the energy needed to release the carriers from the particular trapping level. This is not necessarily the energy needed to raise electrons into the conduction band (or trapped holes into the valence band). Excitation to another level within the forbidden gap might allow recombination, but in this case the carrier cannot migrate far within the crystal and therefore it must be close to its recombination center. For a limited temperature range the carriers are assumed to come from only one trapped level but may recombine at different centers.

Conduction Band

—— N_1
—— N_2
—— N_3

—— M_4
—— M_3
—— M_2
—— M_1

Valence Band

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Fig. 10. A band model scheme for a crystal containing electron trapping levels (N_i) and hole trapping levels (M_j).

1. Glow Curves

The previous discussion suggests that a series of glow peaks would result after irradiating and heating a crystal containing electron and hole traps, and this is indeed the case for dilute concentrations of rare earth ions in CaF_2 . Single crystals of CaF_2 doped with 0.05 - 0.3 wt. % of RE^{3+} were exposed at 77°K to γ -rays from ^{60}Co for periods up to one hour. The crystals were slowly warmed from 100°K to room temperature by means of an adjustable flow of nitrogen gas. The heating rate was not linear but varied from 0.5°/minute in the beginning of the run to 5.0°/minute toward the end of the run. The glow intensity was integrated over wavelength according to the S-20 spectral sensitivity of the photomultiplier (maximum sensitivity at 4100 Å; 50% sensitivity at 3200 Å and 6500 Å), and plotted as a function of temperature. The temperature was measured with a resistance thermometer which gave a linear response in the temperature range 100° - 300°K. Calibration with a Chromel-Alumel thermocouple gave measurements accurate to $\pm 2^\circ$ and precise to $\pm 0.5^\circ$. The resulting glow curves for the rare earths studied are shown in Figure 11. In addition to the actinides, the glow curves for Er, Ho, and Tm are presented for comparison with the lanthanides. The glow curve of an undoped CaF_2 crystal (Optovac) is also shown. Only rough estimates of relative intensities were possible. The Er, Ho, Tm and Am thermoluminescence was so intense that the pen of the recorder was kept on scale by decreasing the anode supply voltage in order to prevent

Fig. 11. Thermoluminescence of $\text{RE}^{3+}\text{-CaF}_2$. All irradiations were at 77°K for 30 minutes in a ^{60}Co source. The dotted lines indicate the positions of glow peak maxima.

saturation of the photomultiplier. This was also necessary for curium because of the ubiquitous orange glow due to self-excited fluorescence. For Np, Pu, and undoped CaF_2 , the thermoluminescence was very weak and the photomultiplier had to be cooled.

The most important fact about the thermoluminescence, evident from the figure, is that the temperatures of the glow peak maxima are essentially independent of the rare earth studied. Although the relative intensities differ, and in some cases are missing, all of the glow curves are similar. The peak temperatures for these glow curves are listed in Table 4. The average temperature for each glow peak is also shown along with the mean deviation from the average. It was not possible to make temperature measurements of the extremely weak emission from neptunium; however, it seems to conform to the other rare earths. Note that even in the case of the undoped CaF_2 some weak peaks are seen. This emission may be from residual rare earth impurities in the crystal or from recombination of electrons and holes formed in the pure material by irradiation. The near coincidence of the glow peaks for all of the rare earths indicates that the mechanism which stimulates emission must be associated with the host crystal rather than the particular rare earth. These results are similar to those obtained by Merz and Pershan⁹⁵ who ascribed the individual glow peaks to the thermal migration of holes within the crystal and their subsequent recombination with divalent lanthanides. However, for the data presented here a new interpretation is obviously necessary. The γ -induced

Table 4. Peak temperatures of glow curves (in °K).

Rare Earths	#1	#2	#3	#4	#5
Cm	146		216 sh	241	269
Pu	140	191	215	237	261 sh
Am	140	193		245	
Ho	140	179	205	243	270
Tm	136	177		240	264
Er	141	183	209	246	270
CaF ₂	141	178		243	
Average	140	183	211	242	267
Mean Dev.	±2	±5	±4	±2	±3

tetravalent Cm, Pu, and Np should be accompanied by the formation of electron traps rather than holes. Arguing in the spirit of Merz and Pershan, thermoluminescence would then be associated with the migration of electrons and their subsequent recombination with the tetravalent ion. This explanation, however, is not satisfactory, since the coincidence of hole migration and electron migration glow peak temperatures (and, implicitly, activation energies) must then be fortuitous. An alternate explanation will be offered in Section IV D-2.

The reproducibility of the Cm glow curves is shown in Figure 12. The three samples have a temperature range of 3° for peak #5 and 5° for peaks # 1 and 4. The most striking feature, however, is that glow peak #5 has a greater relative intensity in the sample which was not exposed to ⁶⁰Co radiation but was damaged "internally" by decay of the Cm nucleus. This effect is undoubtedly related to the relative ease of formation of the defect associated with peak #5.

Thermoluminescence measurements above room temperature were obtained by heating the crystal with a resistance coil and measuring the temperature with a Chromel-Alumel thermocouple. The thermoluminescence spectra of Cm and Am are shown in Figure 13, along with the peak temperatures. Observe that the temperature scale is not linear since the heating rate was not linear. Unfortunately it was not possible to detect the weak thermoluminescence of Np or Pu and hence a comparison with Cm cannot be made. The americium thermoluminescence has only one intense glow peak which corresponds to emission activated by the direct thermal ionization of Am²⁺.⁸⁵ The two weak peaks on the

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Fig. 12. Glow curves for Cm-CaF_2 : a) 2 hours irradiation, photomultiplier cooled; b) 30 minutes irradiation, photomultiplier at room temperature; c) 72 hours self-irradiation, photomultiplier at room temperature.

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Fig. 13. a) Thermoluminescence of Am-CaF_2 . b) Thermoluminescence of Cm-CaF_2 . The temperature scale is not linear.

low temperature side of the main peak suggest the presence of at least two different electron traps; these peaks may correspond to the direct thermal ionization of Am^{2+} in non-cubic sites.⁹⁷

2. Activation Energies

Many different methods of calculating the activation energies associated with thermoluminescence glow peaks have been presented in the literature.¹⁵³⁻¹⁵⁸ Rough estimates of the activation energies, E , for the glow peaks have been made from the data in Figures 11 and 13, using two different methods. First, activation energies were measured from Arrhenius diagrams in which the plot of log of thermoluminescence intensity vs. $1/T$ should give a straight line. The intensity can be written:

$$I = K e^{-E/kT} \quad (9)$$

and hence the slope of the Arrhenius plot is E/k . However, since K is a function of the concentrations of filled and empty traps, the plot is only linear at the beginning of the glow emission when the change in the concentration of trapped carriers can be neglected. An example of using these diagrams to estimate activation energies for Ce is given in Figure 14. The results obtained for many of the rare earths are given in Table 5. The error is often quite large (as much as 25%) because of the difficulty involved in judging the best straight line through the points. In addition, the glow peaks whose leading edge is obscured by overlapping glow peaks could not be directly measured by this method.

Fig. 14. Arrhenius plot for the determination of the activation energy of Cm-CaF₂, peak #1.

Table 5. Activation energies of rare earth glow peaks. Values obtained using Arrhenius diagrams are not in parentheses; values obtained using the method of Halperin and Braner are in parentheses.

Rare Earth	#1 E(ev.)	#2 E(ev.)	#3 E(ev.)	#4 E(ev.)	#5 E(ev.)
Cm	.075 (.071)			.44 (.52)	
Pu	.14 (.21)			(.47)	
Am	(.24)	.11 (.29)		.56 (.51)	
Ho					
Tm					
Er	.11 (.25)	(.35)	(.47)	(.72)	(.73)
CaF ₂	.11 (.14)			.65 (.42)	
Average	.11±.02 (.18±.06)	.11 (.32±.03)	(.47)	.53±.08 (.53±.08)	(.73)

Activation energies were also computed from the formula:

$$E = kT_g^2 / T_2 - T_g \quad (10)$$

where T_g is the temperature of the glow peak maximum and T_2 is the temperature at half-intensity on the high temperature side of peak.¹⁵³ The results using this method are given in Table 5 in parenthesis. These activation energies are admittedly only approximate. More refined techniques are available;^{85,153,154} however, the results exhibit two important facts: similar values for a given glow peak are obtained for different rare earths, and succeeding glow peaks tend toward higher energies. The best evidence for the similarity of the thermoluminescence of different ions is still the glow curves themselves and the quantitative observation that the emission from different ions occurs at identical temperatures.

3. Spectra of the Thermoluminescence

Photographic measurements of the thermoluminescence of Am, Pu and Cm showed that the spectral distribution of the emitted light is characteristic of the rare earth ion, not the host, and corresponds to the fluorescence of the trivalent ion. The weak thermoluminescence of uranium and neptunium, however, could not be recorded.

a. Americium The intense green thermoluminescence of Am-CaF₂ at 500°C has been reported by Edelstein et al.¹³⁷ The emission was found to be characteristic of trivalent Am. According to Merz's mechanism, this high temperature thermoluminescence should correspond to Am³⁺ in tetragonal sites.

The spectra of the thermoluminescence of Am-CaF_2 from 77-300°K was recorded by warming the irradiated crystal in front of the entrance slit of the spectrograph. Since this emission is very weak, the thermoluminescence from three crystals had to be superimposed in order to darken the photographic plate. Figure 15 compares this thermoluminescence with the fluorescence spectrum of $\text{Am}^{3+}\text{-CaF}_2$ in this region taken at 77°K. Although the thermoluminescence lines are considerably broader than the fluorescence lines (due to the higher temperatures involved), it is clear that all of the lines present in thermoluminescence are also present in fluorescence. A single line (at 6928 Å) occurs only in fluorescence which suggests that the thermoluminescence is characteristic of particular site symmetries. This also agrees with Merz's mechanism which proposes that low temperature thermoluminescence is from trivalent ions in cubic sites.

b. Plutonium McLaughlin and co-workers⁹⁴ made crude thermoluminescence measurements of Pu-CaF_2 crystals and found emission bands at ~4800 Å and ~5800 Å. It was suggested that these peaks correspond to the 5200 Å and 6200 Å fluorescence peaks reported for Pu^{3+} in LaCl_3 .¹⁵⁹

c. Curium The thermoluminescence emission spectrum of Cm-CaF_2 from 77° - 300°K and the Hg-excited fluorescence spectrum of $\text{Cm}^{3+}\text{-CaF}_2$ at 77°K are shown in Figure 16. The thermoluminescence is obviously due to the trivalent ion and consists of only three intense sharp lines between 6068 and 6085 Å. It is proposed that at least two of these lines are due to Cm^{3+} ions in cubic site symmetries. The fluorescence

XBL 7111-1659

Fig. 15. Densitometer tracings of photographic plates: a) spectrum of the low temperature thermoluminescence of Am-CaF₂, b) fluorescence spectrum of Am³⁺-CaF₂ at 77°K.

XBL 7111-1661

Fig. 16. Densitometer tracings of photographic plates: a) Hg-excited fluorescence of Cm^{3+} - CaF_2 at 77°K, b) spectrum of low temperature thermoluminescence of $\text{Cm}^{2+}\text{-CaF}_2$.

lines which do not appear in thermoluminescence must then arise from non-cubic sites.

The electronic configuration of trivalent curium is $5f^7$, which makes this ion the simplest of the trivalent actinides. Since the $5f$ shell is half-filled, the ground state is orbitally non-degenerate: $^8S_{7/2}$. The first excited state of Cm^{3+} is $^6P_{7/2}$ at approximately 6000 Å. These levels should actually be described in an intermediate coupling scheme, but the Russell-Saunders designations can be used for convenience. For a cubic crystal field, a $J = 7/2$ level splits into Γ_6 and Γ_7 doublets and a Γ_8 quartet. Selection rules for a magnetic dipole transition allow all but transitions between Γ_6 and Γ_7 . The ground state splittings of Cm^{3+} in cubic sites have been reported by Edelstein and Easley¹⁶⁰ and are shown in Figure 17. The possible electronic transitions for the levels of interest are shown in Figure 18. The maximum number of lines observable is seven. If, however, the spin-lattice relaxation times at the temperatures of interest here are fast, then the dashed lines in Figure 18 would not be observed and the fluorescence would occur primarily from the ground state of the $^6P_{7/2}$ configuration, since the excited levels could relax non-radiatively to the ground level. If Γ_6 is the ground state of the $^6P_{7/2}$ configuration only two intense lines would be observed. It is proposed that the lines observed in thermoluminescence of $Cm-CaF_2$ at 16474.2 and 16461.0 cm^{-1} are due to these transitions since the energy difference of 13.2 cm^{-1} corresponds to the $\Gamma_6 - \Gamma_8$ cubic crystalline field splitting reported by Edelstein and Easley (see figure 17). It is also possible that Γ_8

XBL 74114-1677

Fig. 17. Zero-field energy levels of the $J=7/2$ ground state of Ce^{3+} at cubic sites in CaF_2 . a) and b) correspond to the indicated values of b_4 and b_6 .

XBL 7444-1678

Fig. 18. Allowed dipole transitions for Cm^{3+} in a cubic field (with Γ_6 as the ground state of the $6P_{7/2}$ configuration).

is the ground state of the $6P_{7/2}$ configuration. This might occur if the crystal field splitting of the $6P_{7/2}$ state occurs by a different mechanism from the $8S_{7/2}$ splitting.¹⁶¹ This case is illustrated in Figure 19. The thermoluminescence data can be totally explained by this scheme. The emission line at 16429.0 cm^{-1} corresponds to a transition to the Γ_7 level of the ground state configuration and places this level 45.2 cm^{-1} above the ground state. This agrees with Edelstein's calculation (Figure 17) using $b_6 = -0.1 \text{ cm}^{-1}$.

D. Discussion and Interpretation of Results

Any attempt to explain the experimental data presented in the preceding sections must account for the basic trends which have become evident, as well as include as many of the exceptions or anomalies as possible. The primary concern of this dissertation has been the valence changes which occur in $\text{Ac}^{3+}\text{-CaF}_2$ crystals upon γ -irradiation. Americium, like all of the lanthanides, is partially reduced to the divalent state. All experimental evidence indicated that the reduction mechanism is the same as that proposed by Merz and Pershan. Np, Pu and Cm, however, are partially oxidized to the tetravalent state. High and low resolution absorption studies and thermoluminescence measurements have been made on these ions. In some cases it was not possible to perform a particular experiment on all of the ions (for example, the weak thermoluminescent emission spectrum of Np could not be detected) but in general the ions exhibit the same basic properties and hence will be treated as a single behavioral unit in the following discussion.

XBL 7111-1679

Fig. 19. Allowed dipole transitions for Cm^{3+} in a cubic field (with Γ_8 as the ground state of the $6P_{7/2}$ configuration).

1. Mechanism of Room Temperature Irradiation

Despite the complexity of the irradiation effects, it is now possible to construct an oversimplified and somewhat tentative model by examining the mechanistic implications of the experimental data. Room temperature γ -irradiation of $\text{Ac}^{3+}\text{-CaF}_2$ (here, "Ac" does not include the actinide Am, which shows anomalous behavior) does not affect the majority of ions but converts to the tetravalent state only those ions which have a particular charge-compensating mechanism. This oxidation is accompanied by the release of electrons which become trapped in the lattice resulting in the formation of various defect centers. Such defects can exist in a variety of configurations; two such defects, the F-center and the M-center, have been recently identified.^{109,162}

The mechanism of oxidation is not by direct ionization since the Ac^{3+} decay is not first order. The rate of formation of Ac^{4+} could however, be determined by the limited ability of the lattice to accept extra electrons. In this case the reaction kinetics would not be first order if the lattice becomes saturated with electrons before the supply of reactive Ac^{3+} ions is exhausted. However, since this mechanism predicts that more Ac^{4+} would be formed at 77°K than at room temperature (more electron traps would be stable at 77°K, and the lattice's ability to accept electrons would therefore be increased), it must be rejected because of the contradictory experimental data.

Both the temperature dependence of the Ac^{4+} formation and the non-primary order of the reaction kinetics can be explained if it is assumed that the oxidation mechanism involves the migration of holes.

Gamma irradiation initially results in the formation of electron and hole pairs. Electrons are stripped from interstitial fluoride ions or regular lattice fluorides and are trapped elsewhere in the lattice. Interstitial fluorine atoms and V_K (or similar) centers are left behind. One of these holes may then diffuse to a nearby Ac^{3+} ion and oxidize it by accepting an electron. It should be pointed out that two different types of hole diffusion are involved here. The self-trapped (V_K) hole is simply an electron missing from a lattice fluorine; distortion around that position traps the hole. The hole diffuses by hopping from site to site (a hole hop corresponds to a nearby electron being captured by the hole). The diffusion of an interstitial neutral fluorine, however, involves its actual motion through the lattice. In this model the local environment of the Ac^{3+} does not change if its electron is accepted by a center like the self-trapped hole; however, there will be a change in symmetry if a fluorine atom accepts the electron and remains nearby.

The electrons trapped in the lattice are stable at room temperature but become free to "diffuse" through the crystal as the temperature is increased. When an electron combines with a tetravalent ion, it leaves the ion in a trivalent excited state. The decay of this ion to its ground state results in the observed emission. Since each electron trap configuration requires a different activation energy to free its electron, several thermoluminescence glow peaks are observed. If the defect consists of an electron bound to an anion vacancy (an F-center), the "diffusion" consists of the continual release and recapture of electrons. For other defect configurations the electron may reach the tetravalent ion via the conduction band.

Symbolically, the process of charge oxidation by irradiation and subsequent thermal reduction of the actinide ion can be described as follows. Irradiation at room temperature results in the formation of holes and electron traps:

where X^- can represent either an interstitial or lattice fluoride ion, and X° can represent either a neutral fluorine or some other hole configuration (such as the self-trapped hole, F_2^-). The hole diffuses to the Ac^{3+} ion and accepts an electron:

where the series of dots implies the X° is far from the actinide. Heating after irradiation allows the diffusion of the electrons, e^- , followed by the reduction of the actinide:

The asterisk indicates an excited state of the actinide ion, and ν is the frequency of the photons observed in thermoluminescence.

2. Mechanism of 77°K Irradiation

A model proposed to explain the effects of γ -irradiation at 77°K must incorporate five facts: (1) irradiation oxidizes trivalent actinides to the tetravalent state, but the conversion is not nearly as efficient

as at room temperature; (2) irradiation also produces Ac^{3+} ions with a new charge-compensating mechanism; (3) subsequent heating to room temperature reduces the intensity of both the Ac^{4+} and the new Ac^{3+} (heating to $\sim 400^\circ\text{C}$ completely restores the original spectrum); (4) the temperatures at which this emission occurs are not a property of the particular rare earth (lanthanide or actinide) studied; and (5) the spectrum of the thermoluminescence from 77°K to room temperature corresponds to the fluorescence of the trivalent ion in cubic sites.

The coincidence of the low temperature glow peaks for all of the rare earths studied, regardless of whether they form the divalent or tetravalent state upon γ -irradiation, is obviously the key experimental observation, and any attempt to explain the data must focus attention on this fact. One explanation of the thermoluminescence, first proposed by Arkhangelskaya,⁹⁶ is that γ -irradiation produces pairs of electron and hole centers which do not involve the rare earths. Subsequent heating could cause recombination of these centers with a release of energy sufficient to excite nearby trivalent rare earths, causing them to fluoresce. This possibility, however, must be ruled out because Merz and Pershan observed a decrease in the concentration of the divalent ion which in some cases was proportional to the glow peak intensity. Further EPR work by Tzalmona and Pershan¹⁶³ confirmed the hypothesis that thermal activation of various hole traps is responsible for the observed thermoluminescence in BaF_2 and SrF_2 (and, implicitly, in CaF_2) doped with lanthanide ions.

Merz and Pershan's model suggests the possibility that divalent Np, Pu and Cm are formed in the crystals by γ -irradiation. The process:

might occur independently of the $4+$ formation, or the two processes might be in part related by a γ -induced disproportionation:

Although there is no spectroscopic evidence for the formation of these divalent ions, there exists the possibility that their intense parity-allowed f-d transitions occur in the ultraviolet region and are obscured by the analogous transitions in the $3+$ ions. This, however, is unlikely because the f-d transitions in the lanthanides are known to shift several thousand wavenumbers to the red in going from the trivalent to the divalent ion.¹⁶⁴ Furthermore, comparison of the Am^{2+} spectrum with the Eu^{2+} - CaF_2 spectrum reported by Kaplyanskii and Feofilov¹⁶⁵ shows that they are strikingly similar except that the americium spectrum is shifted approximately 4000 cm^{-1} into the red. The spectra of all of the divalent lanthanides in CaF_2 have been reported by McClure and Kiss.¹⁶⁴ If Np^{2+} , Pu^{2+} and Cm^{2+} follow the example of Am^{2+} , their intense f-d transitions should appear in the visible and near infrared spectral regions and would be easily observable. From these arguments and the data presented in Section IV-B, it must be inferred that the divalent state is not present in these crystals in any significant amount.

The low temperature thermoluminescence cannot be explained by the recombination of electron traps with Ac^{4+} ions since the glow peak temperatures correspond to the migration of holes. This suggests that the thermoluminescence is related to the Ac^{3+} site switches. There is evidence that the site symmetry charges are independent of the Ac^{4+} formation. An obvious mechanism is that one member of a pair (or higher order cluster) of Ac^{3+} ions is oxidized thus changing the electrostatic crystalline field experienced by the neighboring Ac^{3+} ion(s). However, this and similar mechanism which relate the site changes to the oxidation must be ruled out because they posit a unique Ac^{4+} site symmetry which forms at 77°K and not at room temperature. This contradicts the data presented in Section IV-A-1d.

The preceding discussion has contributed to the understanding of the irradiation effects only through negation. The following simple model, consistent with the experimental facts listed in the first paragraph of this section, is proposed. γ -irradiation of $\text{Ac}^{3+}\text{-CaF}_2$ at 77°K has two major effects. The oxidation of Ac^{3+} to the tetravalent state by irradiation has been discussed in the previous section, and the proposed mechanism is still applicable. The relative inefficiency of the oxidation is explained by the immobility of many holes at 77°K; certainly the bulky F° atom cannot diffuse through the lattice at this temperature. The other effect of irradiation is the appearance of Ac^{3+} ions with a new charge-compensating mechanism. Since the usual charge compensators, interstitial fluoride ions and lattice O^{2-} impurities, are most likely immobile at 77°K, it is proposed that the new site symmetry

arises from the localization of an electron near an Ac^{3+} ion which has a non-local compensator. As in Equation 11, γ -irradiation produces holes and electrons. The freed electrons are attracted by the net +1 charge of cubic Ac^{3+} ions and are localized close enough to the Ac^{3+} ion to change its symmetry. Several different configurations (see Figure 20) can exist. When the crystal is heated, the hole centers become free to migrate through the crystal. When a hole approaches a trapped electron, recombination occurs with sufficient energy transferred to the nearby Ac^{3+} to put it in an excited state. The decay of the excited trivalent ion results in the observed cubic thermoluminescence. It should be emphasized that this mechanism, like Merz and Pershan's, is based on the migration of holes and thus accounts for the similarity of lanthanide and actinide glow curves.

Although the proposed mechanism accounts for the effects of irradiation at 77°K, an apparent paradox arises if it is applied to the room temperature irradiation. Since the new Ac^{3+} structure only partially bleaches when the crystal is heated to room temperature, it should also be formed in the room temperature irradiation. This contradicts the data presented in Section IV-A-1c and suggests that competing processes occur. In order for the mechanisms at 77°K and room temperature to be internally consistent, the Ac^{3+} ions which can be oxidized only by irradiation at room temperature must have cubic symmetry. The room temperature oxidation mechanism therefore in part involves the migration of F^0 atoms to cubic Ac^{3+} sites where an electron is transferred from the trivalent ion to the fluorine atom. The newly

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Fig. 20. Possible configurations for the stabilization of an electron near a cubic trivalent actinide ion: a) localization of the electron in a nearest-neighbor interstitial position (the electron could also be localized in a second nearest-neighbor position), b) localization of the electron near Ca^{2+} to form Ca^+ , c) localization of the electron near a lattice F^- to form F_2^- (the electron could also be shared by two F^- ions forming F_3^{2-}).

formed fluoride ion remains near the Ac^{4+} acting as a partial charge compensator. Low temperature irradiation cannot oxidize cubic Ac^{3+} ions because the holes which are mobile at 77°K would leave the Ac^{4+} ion in the extremely unstable condition of being "doubly cubic" (i.e., in need of two compensators).

Using the previously introduced notation, the site symmetry switches at 77°K can be described as follows:

and upon heating the crystal,

3. Supporting Evidence - Color Centers

In addition to the main experimental results of this dissertation, information from the literature on color centers supports the models outlined above. Color centers, induced in the crystals by γ -irradiation, have been attributed to electrons released by Ac^{3+} ions, according to Equation (2), that are trapped in the lattice. Color centers have been intensively studied by optical absorption measurements,^{101,108-112} optical bleaching,^{166,167} and measurements of lattice parameters.¹⁶⁷ This discussion shall be restricted to the case of additively colored crystals (crystals colored by baking in Ca vapor) which possess the

virtue of making it possible to study complexes in which only electrons and vacancies are involved, that is, in which holes are absent. This permits the separation of effects associated with such complexes from those arising from V centers.

Mollwo¹⁰⁸ in 1934 investigated additively colored natural crystals of CaF_2 and found two prominent bands at 3750 Å and 5200 Å, which he called the α -band and the β -band. Mollwo suggested that the α -band was due to the absorption of an F center (an electron trapped at a fluoride vacancy) and it was later shown by Arends¹⁰⁹ that this center exhibits the ESR properties which may be expected for an "F-center-like" color center, viz. a hyperfine structure with approximately the proper theoretical intensity ratios, a negative g-shift independent of the orientation and an inhomogeneous power saturation. FurtherENDOR measurements^{168,169} confirmed the presence of the F-center. Recently it has been shown by Beaumont and Hayes¹⁶² that the α -band is actually a complex superposition of bands arising from the F-center, the M-center and higher F-aggregate centers. It was also shown that the β -band is analogous to the M-center in the alkali halides and consists of two nearest neighbor F-centers (see Figure 21). This center is aligned along a cube edge and has D_{2h} symmetry.

This discussion confirms that the broad absorption bands induced in $\text{Ac}^{3+}\text{-CaF}_2$ crystals by γ -irradiation are indeed due to electrons trapped in the lattice. In Table 3 the bands at ~ 4000 Å correspond to Mollwo's α -band. The exact positions of these bands are difficult to locate because they are masked by the intense f-d transitions

- F^-
- ◻● F^- vacancy
- Ca^{++} above plane of paper
- Ca^{++} below plane of paper

XBL 7111-1664

Fig. 21. Schematic representation of the M-center in CaF_2 .

of the Ac^{3+} ions (see Figure 9); however, the correspondence is still unambiguous. The other intense absorption at $\sim 5800 \text{ \AA}$ probably corresponds to the β -band (the M-center). The maximum wavelength of this band varies slightly from one actinide to another and in all cases occurs at wavelengths greater than $5200 \text{ \AA}$. This discrepancy, however, may be explained by the different methods of color center production. Fong and Yocom¹⁰⁶ found that the coloration of CaF_2 is dependent upon the conditions under which the additive-coloring experiment is conducted. They found β -band absorptions in the region $5200 - 6000 \text{ \AA}$ depending upon the thermal treatment of the crystal. The two weak absorptions at $\sim 8000 \text{ \AA}$ and $\sim 1.05 \mu$ (Table 3) have not been reported in the literature. However, the preceding discussion makes plausible the existence of several types of centers in CaF_2 which are minor variations of the F-center. Electrons could be trapped at different lattice imperfections or at impurity sites, and each would be expected to absorb in a different spectral region. Another explanation that may be offered for the multiple broad absorption peaks is the existence of M-centers in different orientations in the crystal. For example, centers could be aligned along the $[100]$, $[110]$, and $[111]$ crystallographic directions, with a different absorption spectrum for each. However, orientations in different inequivalent directions have not yet been observed for the M-center.

4. Weaknesses of the Model

The model discussed in Section IV-D-2 depends heavily on the result that the low temperature thermoluminescence of $\text{Ac}^{3+}\text{-CaF}_2$ is from cubic sites. The only actinide that could be examined was Cm and the

assignment of the thermoluminescence to a cubic site symmetry was made only indirectly by comparison with ground state cubic crystal field energy levels determined by EPR. It is of course possible that the thermoluminescence results from several site symmetries and the energy difference of the thermoluminescence emission lines fortuitously corresponds to the difference expected for cubic symmetry. Furthermore, although it seems reasonable, the cubic thermoluminescence does not necessarily imply that all of the ions were in cubic sites to begin with. It is possible that some non-cubic ions may undergo symmetry changes, and after the irradiation the charge compensator diffuses away, leaving the ion in a cubic field. This, however, seems unlikely at 77°K in light of the activation energies for F^0 diffusion.^{20,95,170,171}

Another difficulty with the above analysis is the rigorous exclusion of the divalent ion. The question remains whether absorption due to small amounts of Ac^{2+} is masked by color centers.

The presence of impurities in the crystals used for these studies has been noted. However, it must be realized that an exhaustive search for contaminants has not been made, and so the question arises whether impurities could also be responsible for the dominant effects. Perhaps the extremely weak low temperature thermoluminescence of neptunium and plutonium is really due to impurities. This argument certainly has some validity; however, the basic interpretation of the thermoluminescence is not voided because the truly definitive actinide, curium, behaves unambiguously.

According to the high temperature thermoluminescence model proposed in Section IV-D-1, a fluorine atom diffuses toward a cubic Ac^{3+} ion, and acts as a compensator by accepting an electron. These atoms that diffuse thus change their role from non-local compensators to localized ones. During the next irradiation, fewer Ac^{3+} ions would be found in cubic sites so that charge oxidation would not be as efficient. This contradicts the experimental data and the only argument which can be offered is heuristic. Merz and Pershan⁹⁵ suggest that it is possible that after bleaching the crystal relaxes to an equilibrium distribution of localized and non-localized compensators. This means that after recombination, a number of the local interstitial F^- ions are capable of diffusing away from the trivalent actinide. The charge compensators may achieve nearly the same distribution in the lattice each time.

5. Divalency vs. Tetravalency

Whereas all of the lanthanides can be stabilized in the divalent state in CaF_2 , only americium of the actinides forms the divalent state upon γ -irradiation. Trivalent Np, Pu, and Cm are instead oxidized to the tetravalent state.

Since most of the divalent lanthanides have not been observed in solution, their stability in calcium fluoride must be attributed to the intrinsic properties of the lattice. A trivalent ion which replaces Ca^{2+} and has a non-local compensator creates a local charge imbalance. Neutrality can be restored by the capture of an electron by a Ln^{3+} ion (or the localization of an electron by a Ac^{3+} ion, for irradiations at 77°K).

The other property of the CaF_2 lattice which would be expected to help determine which oxidation state is stabilized by irradiation is its size. CaF_2 incorporates RE^{3+} ions easily because they are comparable in size to Ca^{2+} . In Figure 22 the ionic radii of some oxidation states of rare earths are shown and compared with the ionic radius of Ca^{2+} . The lattice might be expected to stabilize those oxidation states which relieve the stress put on the crystal by the incorporation of an ion that is either too bulky or too small. For the lanthanides, however, the size effect cannot be the determining factor since Ce^{3+} , which has a larger ionic radius than any of the actinides studied, is reduced to the divalent state. This would not be expected from spacial considerations alone since an oxidation rather than a reduction would relieve the stress on the lattice. Apparently the $\text{RE}^{3+} + e^- \rightarrow \text{RE}^{2+}$ reduction potentials for the lanthanides are less negative than those for the actinides, since only in the former case is the divalent ion formed.

In the preceding paragraph, the role of the CaF_2 lattice in the formation of the divalent state was attributed to its tendency to restore local charge imbalances created by Ln^{3+} ions in cubic symmetry rather than to spatial considerations. For the actinides, the role of the lattice cannot be attributed to the relief of a charge imbalance, since if anything the imbalance is magnified. In this case the important factor must be the intrinsically greater $\text{Ac}^{3+} \rightarrow \text{Ac}^{4+} + e^-$ oxidation potentials.

XBL 7111-1681

Fig. 22. Ionic radii of rare earth elements¹¹⁹.

6. Uranium

The optical spectra of U-CaF_2 crystals have been the subject of considerable controversy, and the results presented in this dissertation help elucidate the systems. The major confusion seems to be the assignment of the "green" U-CaF_2 crystal. Hargreaves¹⁴⁷ argues that the green crystal is characteristic of divalent uranium in CaF_2 . His assignment results, in part, from an examination of the effects of irradiation on these systems. Since γ -irradiation has been used successfully to partially convert trivalent ions to divalent ions in CaF_2 , Hargreaves irradiated his red U^{3+} and observed a single new absorption band at 6300 Å. In light of the work done on lanthanide ions in CaF_2 , he assigned this new feature to U^{2+} ; however, the results presented in this dissertation suggest that the tetravalent ion is produced by γ -irradiation and that the absorption band at 6300 Å is due to a color center (in particular, the M-center) which results when freed electrons are trapped in the lattice. This assignment is consistent with the recent work of McLaughlin et al.¹²⁸

Hargreaves also examined double-doped crystals containing U^{3+} , Ln^{3+} and large concentrations of Ln^{2+} ($\text{Ln} = \text{Sm}, \text{Nd}, \text{Tm}, \text{or Dy}$). Ultraviolet irradiation of these crystal systems produced more Ln^{2+} but also increased the "green U^{2+} " content. No adequate explanation could be offered; however, the effect is easily explained if the green uranium is indeed the tetravalent ion. An electron is transferred from the U^{3+} ion to the Ln^{3+} ion:

Such reactions have been studied by Feofilov¹³⁰ and, more recently by Welber.¹²⁹

7. Suggestions for Continued Research

The most important direction for a continued effort on these problems is to follow the optical experiments reported here with paramagnetic measurements. The purpose of EPR experiments would be threefold; (1) to identify the symmetry of the tetravalent actinide ion; (2) to study the exact nature of the electron traps formed, in particular the color centers at $\sim 8000 \text{ \AA}$ and $\sim 1.05 \mu$ which have not been previously reported; and, (3) to positively prove or disprove the existence of divalent actinides.

A few experiments should also be mentioned which fall into the category of repeating the measurements reported here with higher accuracy. For example, by using more sensitive detectors, and superimposing several runs, it may be possible to take thermoluminescence emission spectra of Np and Pu. The exact status of U-CaF_2 could also be re-examined and compared with other rare earths.

Undoubtedly the most revealing new experiments would involve detailed optical Zeeman studies of all of the actinides. In this manner, site symmetries could be assigned to many of the optical lines and a more exact model might be proposed. The final section of this dissertation is concerned with optical Zeeman studies, and indeed the motivation was the elucidation of the mechanisms presented above. However, several

problems were encountered which did not allow detailed analyses of the most interesting systems. Higher magnetic fields (via pulsed magnets) and more sensitive detectors should allow site symmetry determinations on more lines.

V. OPTICAL ZEEMAN SPECTRA

It is generally agreed that an examination of the angular dependence of the Zeeman pattern of an optical spectrum line offers the most clearly defined method of establishing the site symmetry of the ion responsible for it. In the usual Zeeman studies, spectra are taken with the magnetic field along important crystallographic directions. In the present case, with a large enough magnetic field to split the lines sufficiently for detailed study, it was decided to take the Zeeman spectra as a function of azimuthal angle about a given crystallographic direction, the magnetic field being maintained in a plane perpendicular to this rotation axis.

The major impetus for this investigation was the elucidation of the effects of radiation on actinide ions in CaF_2 . Unfortunately, it was discovered that the large linewidths of the actinides compared to the lanthanides (due to a greater extension of the 5f orbitals) often limit a study of their Zeeman patterns. Here are presented some preliminary results on americium and curium, and a more detailed investigation of the lanthanide neodymium.

A. Theory

The theoretical interpretation of ions in crystals has been dealt with at length in several textbooks, and will not be developed fully here. The fundamentals of the theory of atomic spectra became understood with the development of quantum mechanics and are presented in the now-classic treatise by Condon and Shortley.¹⁷² The theory was extended by the Hartree-Fock calculations of Slater¹⁷³ for the transition metal

ions. Methods developed by Racah¹⁷⁴ dealt with the more complicated rare earths. Recent books by Griffith¹⁷⁵ and Wybourne¹⁷⁶ on the transition metals and rare earths, respectively, deal with those atoms in great detail. The field has grown to require a high degree of mathematical sophistication: the theory of groups and its application to the interpretation of the spectra of ions in crystals has been treated by several authors;¹⁷⁷⁻¹⁸⁰ crystal field theory is also treated by McClure¹⁸¹ and Ballhausen;¹⁸² the tensor operator methods of Racah along with the theory of continuous groups is given by Judd.¹⁸³ In the following discussion, mention will be made only of the highlights of those theories which will be of concern in the interpretation of the data.

1. General Comments

The Hamiltonian for a system of N electrons about a nucleus of charge Ze is usually treated in the Central Field Approximation. The non-relativistic Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \left(\frac{Ze^2}{r_i} \right) + \sum_{i < j}^N \left(\frac{e^2}{r_{ij}} \right) \quad (19)$$

is replaced by the central field Hamiltonian

$$H_{cf} = -\left(\frac{\hbar^2}{2m} \right) \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i) \quad (20)$$

In this approximation each electron is assumed to move independently in the field of the nucleus plus a spherically symmetric potential $U(r_i)$, which is an average of the potential fields of the other $N-1$ electrons. The Schroedinger Equation resulting from the Hamiltonian of Equation 20 can readily be solved in spherical coordinates. The resulting energy levels are highly degenerate. This degeneracy may be removed by the consideration of a succession of perturbation terms

$$H_p = \sum_i H_i \quad (21)$$

The most fundamental of these perturbation terms is the difference between the Hamiltonians of Equations 19 and 20:

$$H - H_{cf} = \sum_{i=1}^N \left(-\frac{Ze^2}{r_i} - U(r_i) \right) + \sum_{i < j}^N \left(\frac{e^2}{r_{ij}} \right) \quad (22)$$

The first term in Equation 22 shifts all the levels in a given configuration an equal amount, and is therefore usually not of interest. The second term:

$$H_1 = \sum \left(\frac{e^2}{r_{ij}} \right) \quad (23)$$

represents the electrostatic Coulomb interaction among the electrons, and is clearly a two-electron operator. To calculate the effect of H_1

on the one electron states resulting from Equation 20, product states are constructed utilizing the total orbital and spin angular momenta of all the electrons:

$$\vec{L} = \sum_{i=1}^N \vec{l}_i \quad \text{and} \quad \vec{S} = \sum_{i=1}^N \vec{s}_i \quad (24)$$

The resulting energy level diagram consists of a series of multiplet levels designated by ^{2S+1}L .

The next level of approximation for an ion in a crystal considers the perturbation terms

$$H_2 = \sum_{i=1}^N \xi_i \vec{s}_i \cdot \vec{l}_i \quad (25)$$

and

$$H_3 = V_{\text{crystal}} \quad (26)$$

The first of these terms is the spin-orbit interaction; the second is the crystal field perturbation. For the rare earths, due to shielding of the unfilled 4f and 5f shells from their external environment, the spin-orbit term is usually larger than the crystal field perturbation.

If the spin-orbit term is much smaller than the Coulomb interaction, the Russell-Saunders or LS coupling approximation can be used. Taking the total angular momenta S and L as good quantum numbers, Equation 25 can be rewritten

$$H_2' = \zeta \vec{S} \cdot \vec{L}. \quad (27)$$

This Hamiltonian splits the $2S+1L$ multiplet into levels of total angular momentum $J=L+S, L+S-1, \dots, L-S$, each of the J levels being $(2J+1)$ -fold degenerate. This degeneracy can be lifted by other perturbations, such as electric or magnetic fields. However, if H_2 is not small compared to H_1 , then L and S are no longer good quantum numbers. In the limit $H_2 \gg H_1$, the jj coupling scheme is preferable. In the rare earth ions, Russell-Saunders coupling is often a good first approximation, but H_2 is sufficiently large to mix in wavefunctions of other multiplets, and the true coupling is intermediate. The spin-orbit Hamiltonian mixes in states of different S and L , but the same J . The ground state of the ion is usually relatively pure LS coupling, but this coupling breaks down more for the excited states. Furthermore, as the atomic number increases, the spin-orbit parameter ξ_1 increases faster than the electrostatic term, and the breakdown in LS coupling becomes greater.

The general problem of coupling together various angular momenta can best be handled by use of the $n-j$ symbols. In the simplest case of coupling two angular momenta to form a third, the $3-j$ symbol is used. It is related to the customary Clebsch-Gordan or Vector-Coupling coefficients by a simple rotation:

$$\begin{pmatrix} j_1 j_2 j_3 \\ m_1 m_2 m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} (2j_3 + 1)^{-\frac{1}{2}} \begin{pmatrix} j_1 m_1 j_2 m_2 | j_1 j_2 j_3 - m_3 \end{pmatrix} \quad (28)$$

The 3-j symbol is especially useful because it exhibits a great deal of symmetry. To couple three angular momenta together to form a fourth, the 6-j symbol, which can be defined in terms of a sum over 3-j symbols, is needed. For even more complicated cases, the 9-j symbol can be defined in terms of a sum over 6-j symbols. Relations for the various n-j symbols can be found in Edmonds¹⁷⁴ and Judd.¹⁸³ Extensive tables of these symbols have been calculated by Rotenberg et al.¹⁸⁴

For three or more equivalent f electrons, it becomes difficult to classify the states of the system because several terms of a given L and S may occur. In this case the method of continuous groups and the coefficients of fractional parentage becomes extremely useful. Here, the states of an N electron system can be built up from the states of an N-1 electron system, if these are already known.

Another complication which has been neglected in the above discussion is that of configuration interaction. For two configurations of the same parity, interactions can occur between their energy eigenstates. Details of this problem are discussed by Wybourne.¹⁷⁶ In general, however, this effect is not important for the trivalent rare earths since their lowest configurations are usually well separated.

2. Crystal Field Effects

The effect of the crystalline environment on the rare earth spectra can be understood by symmetry considerations through the use of group theory. Each angular momentum eigenvector transforms according to an irreducible representation of the full rotation group in three dimensions. When an atom or ion is imbedded in a crystal, however, the

symmetry at its location is lowered to that of one of the 32 crystallographic point groups. The representation of the full rotation group is then decomposed into the irreducible representations of the point group describing the ion in the lattice. This lifts the degeneracy of the original angular momentum. The rotation representation D_J , which is $(2J+1)$ -fold degenerate, decomposes into the Γ_i representations of the point group under consideration:

$$D_J = \sum_i n_i \Gamma_i \quad (29)$$

where the summation extends over the N irreducible representations of the point group, and the coefficients n_i represent the number of times the representation Γ_i appears in the decomposition of D_J . Because the character of the Kronecker (or direct) product of two representations is the product of the characters of the representations, such decompositions can be constructed from the character tables of the point groups. The procedure is straightforward and the results are tabulated in many books. Perhaps the two most convenient are Prather¹⁸⁵ and Koster et al.,¹⁸⁶ although Low¹⁸⁷ also lists them.

Unfortunately, there is no one standard notation for the labeling of these representations. There is the Hund-Mulliken notation, the Wigner Γ_i notation, and Prather's own modification of the Hund-Mulliken notation. The list does not end here, but these are the common ones. Koster et al.¹⁸⁶ have systematized and extended the Wigner notation and presented it in such a palatable form that it has all but become the standard, at least for physicists, and it will serve as the basic notation for this discussion.

Calculations of the crystal field effects can be made using the method of operator equivalents described by Judd.¹⁸³ The crystal field potential (H_3 in Equation 26) is expanded in terms of the spherical harmonics. These are replaced by operators which transform like the spherical harmonics, and for which matrix elements can be calculated directly. The results of these calculations for a cubic field have been calculated by Lea, Leask and Wolf.¹⁸⁸ Useful results have also been published by White.¹⁸⁹ For the cubic case, the Hamiltonian can be written

$$H_3 = B_4(O_4^0 + 5 O_4^4) + B_6(O_6^0 - 21 O_6^4) = B_4 O_4 + B_6 O_6 \quad (30)$$

Where B_4 and B_6 are fourth-order and sixth-order cubic field parameters, and the O_n^m are angular momentum operator equivalent expressions for the spherical harmonics. Equation 30 is then written

$$H_3 = B_4 F(4) \frac{O_4}{F(4)} + B_6 F(6) \frac{O_6}{F(6)} \quad (31)$$

where $F(4)$ and $F(6)$ are numerical factors common to all matrix elements, and are separated out for convenience. The field parameters B_4 and B_6 are replaced by the substitutions

$$B_4 F(4) = W_x \quad (32)$$

$$B_6 F(6) = W(1-|x|) \quad (33)$$

where $-1 \leq x \leq +1$. The parameter x then measures the ratio of the fourth-order to the sixth-order crystal field, since

$$\frac{B_4}{B_6} = \frac{x}{1-|x|} \frac{F(6)}{F(4)} \quad (34)$$

Thus, B_4/B_6 goes from $-\infty$ to $+\infty$ as x goes from -1 to $+1$. The parameter W represents a scale factor for the energy, and the Hamiltonian can be written

$$H_3 = W \left[x \left(\frac{O_4}{F(4)} \right) + (1-|x|) \frac{O_6}{F(6)} \right]. \quad (35)$$

Lea, Leask and Wolf have calculated the splitting of the crystal field levels for all values of J between $J=2$ and $J=8$ as a function of the parameter x , and the wave functions for these crystal field levels are given as linear combinations of the $|JJ_z\rangle$ eigenfunctions. These results are very useful for estimating the magnitude of the crystal field splitting, the order of the ground state levels, and the relative strength of the sixth order term of the crystal field.

3. Zeeman Effect

The contribution to the Hamiltonian due to an external magnetic field; $\vec{B}$, is given by

$$H_4 = \beta \vec{B} \cdot (\vec{L} + 2\vec{S}) \quad (36)$$

where $\beta = 4.6741 \times 10^{-5} \text{ cm}^{-1}/\text{gauss}$ is the Bohr magneton. In Equation 36 such terms as would be introduced by the quadratic diamagnetic effect, nuclear magnetic moment, nuclear motion and relativistic effects¹⁹⁰ are neglected.

For $\vec{B}$ parallel to $\vec{L} + 2\vec{S}$ (parallel Zeeman effect), Equation 36 reduces to

$$H_{||} = \beta B_z (L_z + 2S_z). \quad (37)$$

For the perpendicular effect, it becomes

$$H_{\perp} = \beta B_x (L_x + 2S_x). \quad (38)$$

It could just as well be $H_{\perp} = \beta B_y (L_y + 2S_y)$ or any linear combination of the two. In fact, $\vec{L} + 2\vec{S}$ transforms as a tensor of rank 1, and it is frequently more convenient to use $B_z (L_z + 2S_z)$ for one component and $1/2 B_+ (L_- + 2S_-)$ and $1/2 B_- (L_+ + 2S_+)$ for the other two. Here $B_{\pm} = B_x \pm iB_y$, and similarly for $L_{\pm}$ and $S_{\pm}$.

For a small enough magnetic field, H_h can be considered as a perturbation on the crystal field levels and the matrix elements of H_h can be calculated using the crystal field wavefunctions. Such calculations have been demonstrated by Koster and Statz.^{191,192}

Rather than work directly with the crystal field wavefunctions, one can employ the basis functions used for computing the crystal field splitting. The matrix elements of interest are

$$\langle \gamma SLJM | L_z + 2S_z | \gamma SLJ' M' \rangle \quad (39)$$

for the parallel effect, and

$$\langle \gamma SLJM | L_{\pm} + 2S_{\pm} | \gamma SLJ' M' \rangle \quad (40)$$

for the perpendicular effect. If we assume no J-mixing, then Equation 39 becomes

$$\langle \gamma SLJM | L_z + 2S_z | \gamma SLJM \rangle \quad (41)$$

and Equation 40 becomes

$$\langle \gamma SLJM | L_{\pm} + 2S_{\pm} | \gamma SLJM \rangle \quad (42)$$

However,

$$\langle \gamma SLJM | L_z + 2S_z | \gamma SLJM \rangle = g(\gamma SLJ) M \quad (43)$$

where $g(\gamma SLJ)$ is the Landé factor. Using crystal field wavefunctions this equation becomes

$$\langle \gamma \Gamma_r | L_z + 2S_z | \gamma \Gamma_r \rangle = g \bar{M}. \quad (44)$$

For Kramer's degenerate levels it is customary to define a parallel splitting factor

$$s_{\parallel}(\gamma \Gamma_r) = 2g \bar{M}. \quad (45)$$

The factor of two makes it convenient, since in actual practice the total separation of the components is measured experimentally.

For the perpendicular effect,

$$\langle \gamma_{JM} | L_{\perp} + 2S_{\perp} | \gamma_{JM \pm 1} \rangle = g[J(J+1) - M(M \pm 1)]^{\frac{1}{2}} . \quad (46)$$

All $\langle \gamma_{JM} | L_{\perp} + 2S_{\perp} | \gamma_{JM'} \rangle$ for $M \neq M \pm 1$ are zero.

For non-cubic crystal fields, if J-mixing is not important, it is convenient to define a perpendicular splitting factor $s_{\perp}$, such that¹⁷⁶

$$s_{\perp} = (J + \frac{1}{2})g .$$

In intermediate coupling the g is the "intermediate coupling Landé g-factor."¹¹

When the parallel and perpendicular splitting values are known for a state, then the splitting factor when the magnetic field is at an angle θ away from the symmetry axis is given by

$$s^2(\theta) = s_{\parallel}^2 \cos^2 \theta + s_{\perp}^2 \sin^2 \theta . \quad (48)$$

4. Selection Rules

Selection rules stem from the symmetry properties of a system and are based on the vanishing of certain matrix elements. If a matrix element, M_{ij}^k , is to be a non-zero scalar, it must belong to the identity representation of whatever group is being considered. Thus if

$$M_{ij}^k = \langle \psi_i^\lambda | Q_k^\mu | \psi_j^\nu \rangle \quad (49)$$

and ψ_i^λ , Q_k^μ , and ψ_j^ν transform according to the Γ_λ th, Γ_μ th and Γ_ν th irreducible representations, respectively, then for M_{ij}^k to be non-vanishing, $\Gamma_\lambda \times \Gamma_\mu \times \Gamma_\nu$ must contain the identity representation Γ_1 .

The inversion operator and its square, the identity, form a two-element group, for which the irreducible representations are Γ_1 , the identity representation, and Γ_2 , the alternating representation. The dipole operator $\vec{P}$ transforms as Γ_2 . Wavefunctions from r^N configurations transform as Γ_1 or Γ_2 , depending on whether N is even or odd. It is apparent that the matrix element $\langle r^N | \vec{P} | r^N \rangle$ is zero, since $\Gamma_2 \times \Gamma_2 \times \Gamma_2$ transforms as Γ_2 , not as the identity representation Γ_1 . Hence electric dipole transitions within the same configuration are not allowed (Laporte's parity rule).

Electric dipole transitions are possible within r^N only if configurations of opposite parity are mixed in, e.g., $r^{N-1}d$. These can be mixed by means of odd elements of the crystal field or by odd vibration modes.¹⁹³ The expansion coefficients of any crystal field in which the point group symmetry included inversion as an element of the group contain no odd elements. Thus intraconfigurational lines involving cubic sites can only be due to magnetic dipole transitions or to forced dipole transitions (The magnetic dipole operator transforms as Γ_1 , so $\Gamma_2 \times \Gamma_1 \times \Gamma_2$ transforms as Γ_1 and the transition is allowed). In C_{4v} symmetry, however, odd elements of the crystal field exist which can mix in the opposite parity higher configurations with the ground configuration.

Thus one could expect strong electric dipole transitions in this case.

The selection rules of concern are those pertaining to transitions between the crystal field states, each characterized by an irreducible representation of the point group symmetry. Such selection rules are easy to derive using the tables of Koster et al.,¹⁸⁶ or they can be taken directly from Prather,¹⁸⁵ who has them already worked out.

The Zeeman selection rules are of considerable interest. For C_{4v} symmetry, with the magnetic field along the symmetry axis, the selection rules are given in Table 6. Of course, if the magnetic field is parallel to one of the tetragonal site axes, it will be perpendicular to the other two. A magnetic field has a symmetry of C_{2h} , and if it is at an angle to the principal symmetry axis, it wrecks havoc with the symmetry. As can be seen from the compatibility tables of Koster et al.,¹⁸⁶ a magnetic field along a 4-fold axis of O_h reduces it to C_{4h} , if along the 4-fold axis of C_{4v} , it reduces it to C_4 , and if along the axis of C_{3v} , the symmetry is reduced to C_3 . But if a magnetic field is applied perpendicularly to the 4-fold axis of C_{4v} or to the 3-fold axis of C_{3v} , the symmetry in both cases is reduced to C_s , which has only a plane of symmetry. The selection rules for such a case are given in Table 7.

Table 6. Polarization selection rules for C_{4v} ($B_1 C_4$ axis).

	Γ_8	Γ_5	Γ_6	Γ_7
Γ_8	π	σ		σ
Γ_5	σ	π	σ	
Γ_6		σ	π	σ
Γ_7	σ		σ	π

Table 7. Selection rules for magnetic fields perpendicular to the principal symmetry axis.

	Γ_3	Γ_4
Γ_3	σ	π
Γ_4	π	σ

B. Experimental

A superconducting magnet was used to study the Zeeman effect. The magnet was built at this laboratory with NbTi 248B ribbon wire obtained from Supercon, on a stainless steel core form $1\frac{7}{8}$ " i.d., $6\frac{1}{2}$ " o.d., and $2\frac{5}{16}$ " thickness. The coil goes normal at 130 A. with a maximum field of 67 kG.

The coil was encased in a cylindrical stainless steel dewar shown in Figure 23. This dewar could hold 20 liters of liquid helium for approximately 36 hours. It was equipped with four quartz windows designed by Mr. Dick Escobales. A cross-section of a window is shown in Figure 24. It is very similar to the one designed by Mollenauer et al.¹⁹⁴ except the Cu-quartz seal is made with Dupont Adiprene L-100. The window is mounted to the dewar wall by means of an Indium wire gasket.

Oriented crystals were mounted in Cu-quartz housekeeper tubes which were in turn connected to a 5' stainless steel rod. The sample was then lowered into the coil from the top of the dewar. The rotation axis was parallel to the given crystal direction and perpendicular to the magnetic field.

Other experimental details were described earlier in Section III.

C. Rotation Patterns

The determination of the site symmetries of the RE^{3+} ions is based on considerations of geometry. The symmetries involved are those of a basic cube.

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Fig. 23. Apparatus used for studying Zeeman effect.

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Fig. 24. Cross-section of quartz window on liquid helium dewar.

Consider first a rotation about the $[001]$ axis. Let 0° azimuth lie along the $[100]$ direction. In Figure 25 the three different tetragonal sites A, B and C are shown with their fourfold axes along the $[100]$, $[010]$ and $[001]$ directions. With the magnetic field at an angle ϕ away from a site axis, the splitting value is given by Equation 48. Table 8 shows the splitting factors of the three equivalent sites for tetragonal symmetry. When the field is in the $[100]$ direction, site A with its fourfold axis parallel to $\vec{B}$ will give rise to a Zeeman splitting of $s_{\parallel}$. Sites B and C with their fourfold axes perpendicular to $\vec{B}$ will give rise to a Zeeman splitting of $s_{\perp}$. When the magnetic field is rotated away from the $[100]$ direction, sites A, B and C become non-equivalent. When $\vec{B}$ is along the $[110]$ direction, sites A and B are magnetically equivalent. Figure 26 shows the pattern expected for $s_{\parallel} > s_{\perp}$.⁶³

The splitting values for trigonal compensation may be worked out in a similar manner. The four equivalent trigonal sites, numbered one through four, correspond to the $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$ axial directions. The resulting pattern is shown superimposed on the tetragonal pattern in Figure 26 for $s_{\parallel}(\text{trigonal}) = s_{\parallel}(\text{tetragonal})$ and $s_{\perp}(\text{trigonal}) = s_{\perp}(\text{tetragonal})$. Observe that sites one and three and sites two and four are magnetically equivalent for all rotations about the $[001]$ axis.

It might appear from Figure 26 that it would be easy to distinguish tetragonal from trigonal symmetry. However, to do so one would have to know not only the vertical alignment of the crystal but also the horizontal alignment, since the angular variation, independent of

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Fig. 25. Tetragonal site axes A, B and C in CaF_2 .

Table 8. Tetragonal splitting factors for rotation about the [001] crystal direction.

		s^2		
		A	B	C
[100]	0°	$s_{\parallel}^2$	$s_{\perp}^2$	$s_{\perp}^2$
[110]	45°	$1/2(s_{\parallel}^2 + s_{\perp}^2)$	$1/2(s_{\parallel}^2 + s_{\perp}^2)$	$s_{\perp}^2$
[010]	90°	$s_{\perp}^2$	$s_{\parallel}^2$	$s_{\perp}^2$
[$\bar{1}10$]	135°	$1/2(s_{\parallel}^2 + s_{\perp}^2)$	$1/2(s_{\parallel}^2 + s_{\perp}^2)$	$s_{\perp}^2$
[$\bar{1}00$]	180°	$s_{\parallel}^2$	$s_{\perp}^2$	$s_{\perp}^2$

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Fig. 26. Theoretical tetragonal and trigonal splitting values for rotation about $[100]$ direction.

phase, is the same for both symmetries. Furthermore, it would be necessary to distinguish the isotropic line due to tetragonal site C from a cubic line.

Considering next a rotation about the $[111]$ axis, it can be shown that, except for an isotropic trigonal line, the angular variation is the same for both tetragonal and trigonal symmetries.

For a rotation about the $[\bar{1}10]$ axis, however, there is a striking difference in the angular variation of tetragonal and trigonal splitting factors. Figure 27 shows the splitting pattern expected for $s_{\parallel}(\text{tetragonal}) = s_{\parallel}(\text{trigonal}) \rangle s_{\perp}(\text{tetragonal}) = s_{\perp}(\text{trigonal})$.⁶³ Note that there are two tetragonal lines and that their behavior is not identical. Successive minima are equal; the maxima alternate in magnitude. Also, there is a $70^{\circ} - 110^{\circ}$ split between those angles at which the tetragonal lines merge. There are three trigonal lines, two of which behave alike. The minima for all three are equal and occur in triples 55° apart, followed by a gap of 70° . The two primary maxima occur 70° apart.

In the above discussion only the splitting patterns for tetragonal and trigonal symmetries were considered, since these are the most common sites found in $\text{RE}^{3+}\text{-CaF}_2$ crystals. Fong and Wong¹⁹⁵ have worked out the patterns expected for C_{2v} symmetry and more recently Fong and Bellows¹⁹⁶ have published the patterns for C_2 symmetry. These patterns are extremely complex due to the large number of equivalent sites.

In EPR one can measure the splitting of a single Kramer's degenerate level directly, exciting magnetic dipole transitions between its two components. In optical spectra, the transitions are between

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Fig. 27. Theoretical tetragonal and trigonal splitting values for rotation about $[110]$ direction.

Stark components of different levels and the resulting lines are functions of the splitting of both levels. Thus, whereas in the most general orientation there are three tetragonal EPR lines, each zero field tetragonal optical line splits into 12 Zeeman components. If L denotes the lower level and U denotes the upper level, then the tetragonal lines are $X(L \rightarrow U', L \rightarrow U, L' \rightarrow U', L' \rightarrow U)$, $Y(L \rightarrow U', L \rightarrow U, L' \rightarrow U', L' \rightarrow U)$, and $Z(L \rightarrow U', L \rightarrow U, L' \rightarrow U', L' \rightarrow U)$ where the prime indicates the upper Zeeman component. For the trigonal case, the lines are $1(L \rightarrow U', L \rightarrow U, L' \rightarrow U', L' \rightarrow U)$ and similarly for sites two, three and four. For the magnetic field along certain crystal directions, the splitting factors become equal for all of the sites, and as a result the lines due to the several sites coalesce into one set of four, corresponding to the four possible transitions between two sets of Kramer's doublets. This is illustrated in Figure 27, where it is shown that all of the trigonal lines coalesce when the magnetic field is in the [001] direction.

If absorption spectra are taken at liquid helium temperature, a large enough magnetic field will "freeze out" half of the Zeeman pattern components, namely those arising from L' , leaving only those arising from L, the lowest level of the ground manifold.

Figure 28 illustrates the complete optical Zeeman rotation pattern expected for a case $a_{\parallel}(L) > a_{\perp}(L)$, $a_{\parallel}(U) < a_{\perp}(U)$, where the site symmetry is tetragonal and the rotation is about the $[\bar{1}10]$ axis. Each group of lines in this pattern, of course, has the same shape as the tetragonal splitting value pattern of Figure 27.

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Fig. 28. Theoretical optical Zeeman rotation pattern for tetragonal symmetry, rotation about $[110]$ direction.

It is apparent from a comparison of the two patterns of Figure 27 that the angular variation of the Zeeman pattern of a trigonal site is so different from that of a tetragonal site that if the whole pattern is found there should be no difficulty in distinguishing between them. The trouble is that the whole pattern (or even half of the pattern, at liquid helium temperature) is rarely present. Lines are frequently missing, or if present are very weak. Also, and even more troublesome, there is frequently a host of other lines mixed in with the pattern, obscuring and confusing it.

If the pattern is complete, one can obtain the splitting factors of both the upper and lower levels involved in the transitions. In these studies, however, the pattern was rarely complete, and while the gross angular variation of the Zeeman pattern allowed the site symmetry determination of a number of lines, the splitting values could not be measured with assurance.

D. Discussion of Results

1. Americium

The electronic configuration of trivalent Am is $5f^6$ which makes it the only ion to be studied in this section which is not Kramer's degenerate. The ground state is a singlet, 7F_0 , and hence the Zeeman rotation pattern is simplified. The most intense transition occurs at approximately $20,000\text{ cm}^{-1}$ (5000 Å) and corresponds to a transition to an excited state with $J = 6$. This state has predominately 5L_6 character mixed with some 5G_6 .¹⁹⁷

It was possible to obtain the optical Zeeman rotation pattern for only one Am^{3+} absorption line. The other lines were either too weak, too broad, or did not exhibit any splitting. The observed rotation pattern for the line at 5223 Å is shown in Figure 29. It is apparent from the angular variation that the symmetry of the line is tetragonal. Note in particular the characteristic $70^\circ - 110^\circ$ split between the angles at which the lines merge. Further comparison with the splitting value pattern of Figure 27, however, shows that the pattern is not ideal. This might be explained by a gross misalignment of the crystal, but this is unlikely since the rotation line which corresponds to site A = site B would then be expected to split into two lines. A more likely explanation is that another tetragonal line lies nearby. In this case the magnetic splitting of the absorption lines would be of the same order of magnitude as the Stark splitting and the first order approximation would no longer be sufficient. This effect is in many ways analogous to the Paschen-Bach effect, although not identical with it.¹⁹⁸ This explanation is indeed feasible since four weak Am^{3+} absorption lines were observed 2.4, 2.7, 5.1 and 12.4 cm^{-1} from the intense line. Furthermore an asymmetry in the observed pattern supports this explanation since the Zeeman effect becomes non-linear when the first order approximation breaks down.

Although only a single line could be investigated, valuable information was gained about the thermoluminescence discussed in Section IV-C-3a. This absorption line at 5223 Å corresponds to one of the high temperature thermoluminescence emission lines observed by Edelstein,

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Fig. 29. Optical Zeeman rotation pattern for $\text{Am}^{3+}\text{-CaF}_2$, rotation about $[110]$ direction.

Basley and McLaughlin,¹³⁷ and hence confirms Marz's proposal that such thermoluminescence is due to tetragonal sites.

2. Curium

The electronic configuration of Cm^{3+} is $5f^7$. The $5f$ shell is half-filled and hence the ground state is orbitally non-degenerate, $^8S_{7/2}$. The first excited state of Cm^{3+} ($^6P_{7/2}$ at $\sim 6000 \text{ \AA}$) is the level of interest since it was postulated in Section IV-C-3c that the lines at 16474 and 16461 cm^{-1} (and possibly the line at 16429 cm^{-1}) are due to the ion in cubic site symmetry.

The absorption and fluorescence of Cm was taken with a 3.4 meter Ebert spectrograph in ninth order. The reciprocal linear dispersion was $\sim 0.7 \text{ \AA/mm}$. The absorption of Cm^{3+} at $\sim 6000 \text{ \AA}$ is very weak and only one line at $6063.2 \text{ \AA}$ was intense enough to follow. Its $[110]$ rotation pattern is shown in Figure 30. Although all of the Zeeman components do not unambiguously form a pattern, the pattern at the bottom of the figure is obviously tetragonal (compare with Figure 27). The $[100]$ rotation pattern for this line was also measured and is shown in Figure 31. Two groups of Zeeman components are present which correspond, in the notation of Figure 28, to the transitions $L \rightarrow U$ and $L \rightarrow U'$; however, only the latter transition has a distinct pattern. It is similar to the theoretical pattern shown in Figure 26 except that the isotropic line with the splitting factor s_1 (site C) is missing. Also missing are the Zeeman components due to sites A and B when they approach the orientation condition site A (site B) = site C. The absence of these components cannot be explained by the selection rules, since, as is shown in Table 7,

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Fig. 30. Optical Zeeman rotation pattern for Gd^{3+} - CaF_2 , rotation about $[110]$ direction.

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Fig. 31. Optical Zeeman rotation pattern for $\text{Cm}^{3+}\text{-CaF}_2$, rotation about [100] direction.

all transitions are allowed when the magnetic field is perpendicular to the principal symmetry axis. Of course, the non-vanishing of certain matrix elements does not guarantee that their magnitude will be great.

The [100] Zeeman rotation pattern also taken in fluorescence. The most intense lines at 6000 Å and 6020 Å (see Figure 16) are very broad and hence do not show a resolvable pattern. The only line which was sharp and intense was again the line at 6063.2 Å. The fluorescence pattern was found to be identical to the absorption pattern. The photographic plate is shown in Figure 32. Observe that the "cubic" lines are too weak to follow.

3. Neodymium

Although trivalent neodymium has been incorporated into a large number of crystals, the only ones which have been fully investigated are CaWO_4 ,¹⁹⁹⁻²⁰¹ PbMoO_4 ,²⁰² and LaF_3 .²⁰³

The site symmetries of Nd^{3+} in CaF_2 have been investigated mainly by electron paramagnetic resonance. Bleaney, Llewellyn and Jones²⁰⁴ observed Nd^{3+} in tetragonal sites with $g_{\parallel} = 4.412$ and $g_{\perp} = 1.301$. Kisk and co-workers²⁰⁵ later observed two kinds of orthorhombic symmetry in addition to tetragonal symmetry. They found that the intensity of the orthorhombic symmetry increases with Nd^{3+} concentration. Another group of workers²⁰⁶ have observed Nd^{3+} in cubic sites.

There have also been a number of investigations of the optical spectrum of Nd^{3+} - CaF_2 . Kiss²⁰⁷ attempted to compare the observed absorption spectrum with the theoretical spectrum based on the assumption of a cubic field. Voronko et al.²⁰⁸ analyzed the optical spectrum of

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Fig. 32. Photographic plate of optical Zeeman spectra in fluorescence, rotation about $[100]$ direction. Spectra are taken at 15° intervals; the reference spectrum is neon.

Nd^{3+} - CaF_2 by the concentration series method and were able to group together lines belonging to three different sites. The actual assignments of the symmetries were based on correlations with EPR data.

For the $4f^3$ configuration of Nd^{3+} , there are 17 possible terms, denoted by $^2P_{2D}2F_{2G}2H_{1K}L$ and $^4S_{4D}F_{4G}I$.³⁷ The number of levels with different values of J is 41. The ground state is $^4I_{9/2}$. When an ion is embedded in a crystal, the spectral positions of the absorption groups are known to be quite consistent with the transitions of the free ion.^{208,209}

Crystals of Nd^{3+} - CaF_2 containing from 0.01 - 0.3 wt. % Nd were obtained from Optovac, Inc.¹¹⁷ The following is a study of the Zeeman effect on some selected transitions.

a. $^2H_{11/2}$ The $^2H_{11/2}$ manifold occurs at $\sim 16,000 \text{ cm}^{-1}$ (6250 Å). For the 0.01 and 0.03 wt. % crystals, only one intense absorption line (6263.2 Å) is present. The rotation pattern on this line is not complete -- some Zeeman components are either missing or weak at these concentrations. In order to intensify these weak components, a more concentrated crystal (0.3 wt. %) was studied. The optical rotation pattern for this crystal is shown in Figure 33. Instead of the 6263.2 Å line becoming more intense, it decreased slightly in intensity and a new line at 6253.5 Å grew in. The pattern of the 6263.2 Å line is still not complete but obviously is tetragonal. The line at 6253.5 Å is not tetragonal but exhibits an extremely complex rotation pattern suggestive of a low crystal symmetry. This line could possibly be orthorhombic (C_{2v}) since the EPR measurements of Kask *et al.*²⁰⁵ found that at low

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Fig. 33. Optical Zeeman rotation pattern for 0.3 wt. % Nd³⁺-CaF₂, rotation about $[\bar{1}10]$ direction ($2H_{11/2}$ manifold).

concentrations the tetragonal symmetry predominates, but the intensity of the orthorhombic signal increases with the Nd^{3+} concentration.

b. $^4\text{S}_{3/2}; ^4\text{F}_{7/2}$ The Zeeman rotation spectra for the absorption lines at $\sim 7300 \text{ \AA}$ are shown in Figure 34. At first glance it would seem that the patterns are almost ideal. Only a few Zeeman components are missing and all of the lines can be fit on well-shaped tetragonal patterns. Two zero field absorption lines at $7262.0 \text{ \AA}$ (13767 cm^{-1}) and $7267.2 \text{ \AA}$ (13757 cm^{-1}) split into four tetragonal patterns. Thus for both lines the transitions $\text{L} \rightarrow \text{U}$ and $\text{L}' \rightarrow \text{U}'$ are well-defined. The relation of the zero field lines to the Zeeman components can be seen in Figure 35. This shows the splittings of the lines as a function of magnetic field strength. Note that the Zeeman components of the two tetragonal lines repel one another as the magnetic field is increased. This interaction can be thought of as a "crystal Paschen-Bach effect" and can happen with closely spaced Stark levels in a large enough magnetic field. The effect of this interaction on the rotation patterns can be seen in the asymmetry of the patterns about the zero field lines. At greater magnetic field strengths or with smaller Stark splittings, it is possible for the Zeeman components from different zero field lines to cross, thus creating a confusion interchange in the normal pattern order.

In addition to the lines at 7262 and $7267 \text{ \AA}$, another tetragonal line was found at $7356 \text{ \AA}$. These assignments confirm the work of Voronko et al.²⁰⁸ who, using the concentration series method, assigned lines at 7267 and $7256 \text{ \AA}$ to tetragonal site symmetry.

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Fig. 34. Optical Zeeman rotation pattern for 0.1 wt. % $\text{Na}^{3+}\text{-CaF}_2$, rotation about $[110]$ direction ($^4\text{S}_{3/2}$; $^4\text{F}_{7/2}$ manifold).

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Fig. 35. Splitting of absorption lines as a function of magnetic field strength ($^4S_{3/2}; ^4F_{7/2}$ manifold).

C. $^2H_{9/2}; ^4F_{5/2}$ Only one absorption line at 7962 Å (12556 cm⁻¹) could be followed in this spectral region. Although the symmetry is obviously tetragonal (see Figure 36), the pattern is not ideal. This line probably corresponds to the tetragonal line at 7960 Å reported by Voronko et al.;²⁰⁸ however, they reported another nearby line at 7264 Å whose symmetry is orthorhombic.

E. Conclusions and Recommendations

The optical Zeeman rotation patterns have been taken of CaF₂ crystals containing Am³⁺, Cm³⁺ and Nd³⁺. In all three crystals only sites arising from tetragonal compensation could be positively identified, although there was evidence that lower symmetries exist at high concentrations of Nd³⁺. Only one tetragonal line could be identified for Am³⁺-CaF₂ and for Cm³⁺-CaF₂; five tetragonal lines were identified for Nd³⁺-CaF₂.

This technique allows the positive identification of the site symmetry, whereas the other methods outlined in Section IC do not. It is applicable to all crystal systems containing non-equivalent sites which have spectral lines sharp enough to allow resolution of their Zeeman components.

The sensitivity of the technique could be improved in several ways: 1) larger magnetic fields could be attained using pulsed magnets; 2) thicker crystals of a given concentration could be grown thus increasing the intensity of the absorption lines without changing the site symmetry distribution; 3) a more sensitive detection device could be

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Fig. 36. Optical Zeeman rotation pattern for 0.1 wt. % Nd^{3+} - CaF_2 , rotation about $[110]$ direction ($^2\text{H}_{9/2}$; $^4\text{F}_{5/2}$ manifold).

used, allowing weak fluorescent Zeeman components to be recorded;

4) spectra could be taken in 5° increments, allowing rapidly changing Zeeman components to be followed; and 5) several crystals could be grown under different conditions. This might change the site symmetry distributions so that a single site would predominate in a given spectral region.

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