

determine the symmetry at the rare-earth site during the recombination event, it has been possible to formulate a model which assigns particular properties to the different hole centers. The absorption data demonstrated that these hole centers definitely exist and the holes and divalent ions bleach simultaneously as the temperature is increased. The model described in the Introduction was then shown to explain most of this absorption and thermoluminescence data. Additional evidence was cited from the literature to support this model. The centers proposed to be responsible for these effects involve different configurations of the F_2^- molecular ion, but the model does not attempt to describe the actual configuration associated with each glow peak. Detailed studies of the V_K and related centers in CaF_2

are still to be pursued. It would be interesting to study the implications of the phenomena described here to the theory of small polarons. This has also been pointed out by Keller and Murray for the case of KI .⁷⁰

ACKNOWLEDGMENTS

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Charge Conversion of Irradiated Rare-Earth Ions in CaF_2 . II. Thermoluminescent Spectra*

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High-resolution emission spectra are observed for individual glow peaks from all the lanthanide ions in CaF_2 . The crystals are irradiated with x rays (or γ rays) at 77° and subsequently heated. For a given ion, identical spectra are observed for all glow peaks below 300°K . In all cases where the spectra can be interpreted, the ions responsible for these glow peaks are in sites of cubic symmetry. For some of these ions this is the first time that cubic emission has been seen without the complication of accompanying emission from sites of lower symmetry. The emission above room temperature is always from ions of axial symmetry, which for Gd^{3+} has been identified as tetragonal. Comparison is also made between Gd^{3+} in CaF_2 , SrF_2 , and BaF_2 . In the last two cases both cubic and trigonal symmetry are observed below room temperature.

I. INTRODUCTION

THE preceding paper¹ (henceforth to be denoted as I) described studies of the x-ray-induced (or γ -ray-induced) reduction of trivalent rare-earth ions in CaF_2 single crystals at 77°K and their subsequent thermal oxidation on heating. Changes in optical absorption spectra that accompanied peaks in the "glow curves" were monitored and a model of the electronic processes was proposed. To a large extent that model made use of the emission spectra to be reported in this paper.

Unusually high-resolution thermoluminescent spectra were obtained for low-radiation dosages by using a slow heating rate and a cooled photomultiplier. The spectra of individual glow peaks could be recorded by heating the crystal slowly (after irradiation) and scanning the spectrometer through each glow peak one or more

times. For all but the weakest of peaks several passes could be made and the results of each compared. Since the total emission of the glow peak, integrated over wavelength, was being monitored at the same time, relative changes in the intensities of emitted lines during the course of a single glow peak could be monitored, as well as changes from one glow peak to the next. When the spectra for several passes through the same glow peak were normalized to a standard value (usually the maximum of the integrated glow peak), no changes in the spectral distribution of the emission were seen, to within the accuracy of the intensity measurements (approximately 10%). Thus, the spectra were found to be relatively "pure"—different species of ions emitting at different rates were never found within a single glow peak. However, important differences in the spectra were found from one glow peak to another. In general, these were differences in the site symmetry of the emitting trivalent rare-earth ion. For most of the glow peaks below room temperature the rare earth is found in a cubic site. In some cases, where the transition probability for such emission is strongly forbidden, all the emission consists of vibrationally induced transitions. The large glow peak that is found for most of the rare earths at about 330°K consists of trivalent

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¹ J. L. Merz and P. S. Pershan, preceding paper, *Phys. Rev.* **162**, 217 (1967).

ion emission from tetragonal sites. In view of the fact that trace amounts of rare-earth ions in lower symmetry often dominate the fluorescence emission of rare-earth ions in CaF_2 crystals, the procedure of irradiation at low temperature followed by heating provides a unique opportunity to study the cubic emission spectra.

In Sec. II the experimental procedure is described briefly. The spectra are presented in Sec. III and discussed in Sec. IV. In Sec. V a brief comparison between the emission spectra of Gd in CaF_2 and its isomorphs is presented.

II. EXPERIMENTAL PROCEDURES

Two different instruments were used for spectral measurements during the course of this work. For high-irradiation dosages (including exposure to γ rays), spectra were photographed on Kodak spectroscopic plates or Polaroid film using a Jarrell-Ash 3.4-m Ebert spectrograph, Model 70-000. For the weaker emission resulting from low dosages of x rays, photoelectric detection was employed using a cooled 1P28 photomultiplier in conjunction with a Jarrell-Ash 0.5-m Ebert spectrometer, Model 82-000, with an 1180 groove/mm grating.

The procedure generally employed with the photoelectric system was as follows. A fresh crystal was irradiated, and the spectra of the glow peaks was measured with relatively low resolution between 6000 and 3000 \AA . These low-resolution measurements established the wavelength ranges where emission occurred. The sample was then reirradiated, and a narrow spectral range chosen for high-resolution measurements. Multiple scans of this emission could be made for a given glow peak. The maximum resolution used depended on the particular ion being studied, but was often better than 1 \AA . This was usually sufficient to resolve crystal-field splittings, so that differences in the environment of the rare-earth ions contributing to different glow peaks could be detected. The sample could be reirradiated as often as necessary to study other emitting levels.

The method used for cooling the RCA 1P28 photomultiplier was based on a technique described by Marrinan.² The photomultiplier and voltage divider were mounted inside a pyrex Dewar, filled with liquid nitrogen to a level just below the photomultiplier. The resulting gas cooling was enhanced by immersion into the liquid nitrogen of the electrostatic shielding which was in electrical and thermal contact with the photocathode. This resulted in a decrease of dark current by better than a factor of 10^3 , and signals of a few μA were detected.

For a few of the ions, spectral measurements were made photographically. In these cases, the shutter was left open during the emission time of a given glow peak, and the camera was then racked to another position to

record the emission of the next peak. Photographic data therefore integrate over time, and contain no information about changes during a given glow peak. Densitometer traces were recorded for all photographic data.

For comparison with the thermoluminescent spectra, fluorescence measurements could conveniently be made with either of the two Jarrell-Ash spectrometers. A 90-W Philips high-pressure mercury lamp with a quartz envelope was usually used as the excitation source. Source light was eliminated at the detector using complementary Corning filters in the usual manner.

III. THERMOLUMINESCENT SPECTRA

A survey of the thermoluminescence of each of the rare earths in CaF_2 was recorded photographically using low dispersion prism spectrographs. Measurements were made between 14 000 and 43 000 cm^{-1} on CaF_2 crystals doped with each of the twelve rare earths, CaF_2 doped with yttrium, and undoped CaF_2 . In each case the observed sharp line spectrum was characteristic of the rare earth. Comparison with the energy-level diagram for trivalent rare-earth ions³ showed that the rare-earth levels observed in fluorescence also appear in thermoluminescence. This was verified by fluorescence measurements on the same samples.

A common contaminant in rare-earth-doped CaF_2 is yttrium⁴; the thermoluminescence of a sample containing 0.05% Y was therefore measured. The sharp line structure characteristic of the rare earths was not observed; nor were the lines that have been attributed to recombination from highly associated electron-hole pairs.⁵ Instead, a broad emission band through most of the ultraviolet appeared. For a few of the rare earths, such as Pr, Eu, and Gd, a weak emission band was seen from about 23 000 cm^{-1} extending into the uv. The undoped crystal also showed some broad emission bands in the uv. The presence of such emission would be expected from the integrated thermoluminescence of undoped CaF_2 discussed in I. This emission could originate either from residual impurities in the lattice or from recombination of holes formed during the irradiation. This problem will be discussed after the high-resolution data have been presented. Despite the presence of these weak uv bands in some of the samples, the dominant thermoluminescence corresponds to the fluorescence of the trivalent rare-earth ions. This is evident from the high-resolution thermoluminescent spectra presented below.

A. Gadolinium

The electron configuration of Gd^{3+} is $4f^7$, which makes this one of the simpler of the trivalent rare-

³ G. H. Dieke and H. M. Crosswhite, *Appl. Opt.* **2**, 675 (1963).

⁴ J. R. O'Connor and J. H. Chen, *Phys. Rev.* **130**, 1790 (1963).

⁵ J. R. O'Connor, *Appl. Phys. Letters* **4**, 126 (1964).

² H. J. Marrinan, *J. Opt. Soc. Am.* **43**, 1211 (1953).

earth ions. Since the $4f$ shell is half-filled, the ground state is orbitally nondegenerate: $^8S_{7/2}$. Crystal-field splitting of this ground state⁶ is less than 2 cm^{-1} and is too small to be resolved in these measurements. The lines observed can therefore be attributed to crystal-field splittings of the excited levels. The first two excited states of Gd^{3+} are $^6P_{7/2}$ at approximately 3120 \AA and $^6P_{5/2}$ at 3055 \AA . The fluorescence spectra of Gd^{3+} in CaF_2 has been studied by Makovsky,⁷ who was able to establish which lines were being emitted from Gd^{3+} ions in sites of cubic, tetragonal, and lower symmetry. These sites were then associated with the various types of charge compensation discussed in I. The spectra measured by Makovsky has also been reported by Gilfanov and co-workers.⁸

The thermoluminescence measurements for 0.03% gadolinium are shown in Fig. 1. A spectrum is presented for each of the major glow peaks, and comparison is made with the fluorescent data of Makovsky. For all of the glow peaks below room temperature, labeled No. 1 through No. 4, identical emission from the $^6P_{7/2}$ level is observed. This spectrum consists of three sharp lines between 3110 and 3120 \AA , and agrees with Makovsky's identification of the emission of Gd^{3+} from a site of cubic symmetry. Three lines would be expected for a cubic field, since a $J = \frac{7}{2}$ level splits into a quartet (Γ_8) and two doublets (Γ_7 and Γ_6).

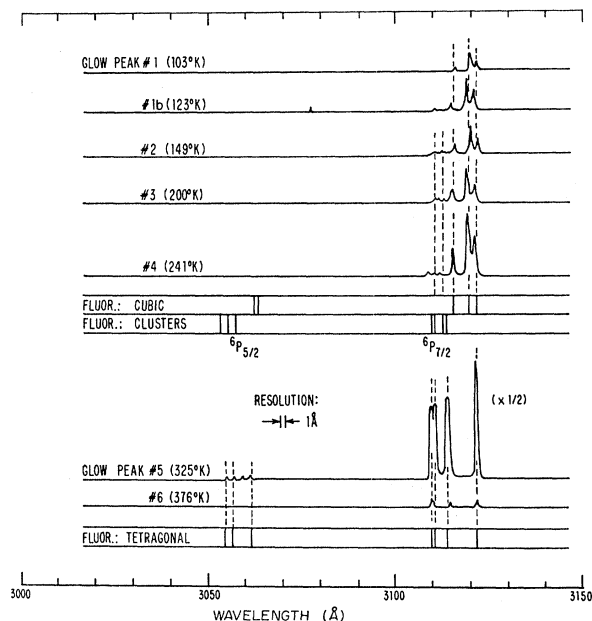


FIG. 1. Thermoluminescent spectra of 0.03% gadolinium. Fluorescence of these ions in various sites is indicated by the bar graphs (Ref. 7).

⁶ J. Sierro, *Phys. Letters* **4**, 178 (1963).

⁷ K. Makovsky, in *Proceedings of the Physics Quantum Electronics Conference*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966); *Phys. Letters* **19**, 647 (1966).

⁸ F. Z. Gilfanov, Zh. S. Dobkina, A. L. Stolov, and L. D. Livanova, *Opt. i Spektroskopiya* **20**, 283 (1966) [English transl.: *Opt. Spectry. (USSR)* **20**, 152 (1966)].

The results clearly establish that the emission from all the peaks below room temperature is predominately from sites of cubic symmetry. Weak emission from clusters of gadolinium ions also appears, and this was seen to grow with increasing concentration.

The peaks above room temperature, on the other hand, come from sites of tetragonal symmetry, where the quartet splits into two doublets separated by 1.5 \AA and four lines can be seen. For the strong glow peak at 325°K some weak emission is also observed from the $^6P_{5/2}$ state, which splits into three doublets under tetragonal symmetry. In addition, a broad-band emission was seen in each of these runs from 3300 to 4500 \AA , peaking at about 3700 \AA . However, the intensity at the peak of this band was only 1% of the gadolinium emission.

Two different symmetry sites have therefore been observed in the thermoluminescent spectra of gadolinium in CaF_2 . All the glow peaks below room temperature originate from Gd^{3+} in cubic sites, while the higher-temperature peaks display tetragonal symmetry. These symmetry identifications could be established in gadolinium because of the simplicity of the spectra. Evidence for this same behavior recurs in the other ions studied.

B. Praseodymium

Spectral measurements on a sample doped with 0.09% praseodymium are shown in Fig. 2. For the low-temperature glow peaks, emission between 4700 and 5100 \AA is divided into two sets of lines, denoted by $L_1^{(2)}$ and $L_0^{(2)}$. These are believed to correspond to emission from the 3P_1 and 3P_0 states, respectively. For the higher-energy state 3P_1 , the four lines observed can be fitted to the spectrum expected for a cubic crystal field. The 3P_1 level transforms according to the Γ_4 representation of the octahedral group, and is therefore not split by the cubic field. The ground state of Pr^{3+} is 3H_4 , which splits into $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. None of the transitions between these levels and the excited Γ_4 level are forbidden for a magnetic dipole transition, so four lines are expected. Four lines are actually seen, labeled $L_1^{(1)}$ through $L_1^{(4)}$, and they can be described by results derived by Lea, Leask, and Wolf⁹ (henceforth referred to as LLW) for a $J = 4$ level in a cubic crystal field. The best fit occurs at $x = 0.98$ ($-1 \leq x \leq 1$; cf. LLW or Ref. 10 for definition of x), which makes Γ_5 the lowest level, and the other levels are ordered as shown in Fig. 2. Weber and Bierig list a value of $x \approx 0.9$ from estimated crystal-field parameters. These large values of x mean that the effect of the sixth-order term in the cubic field expansion is small.

The spectrum is harder to interpret for the transition from the 3P_0 level, which transforms according to the Γ_1 representation. Selection rules allow magnetic (and

⁹ K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids* **23**, 1381 (1962).

¹⁰ M. J. Weber and R. W. Bierig, *Phys. Rev.* **134**, A1492 (1964).

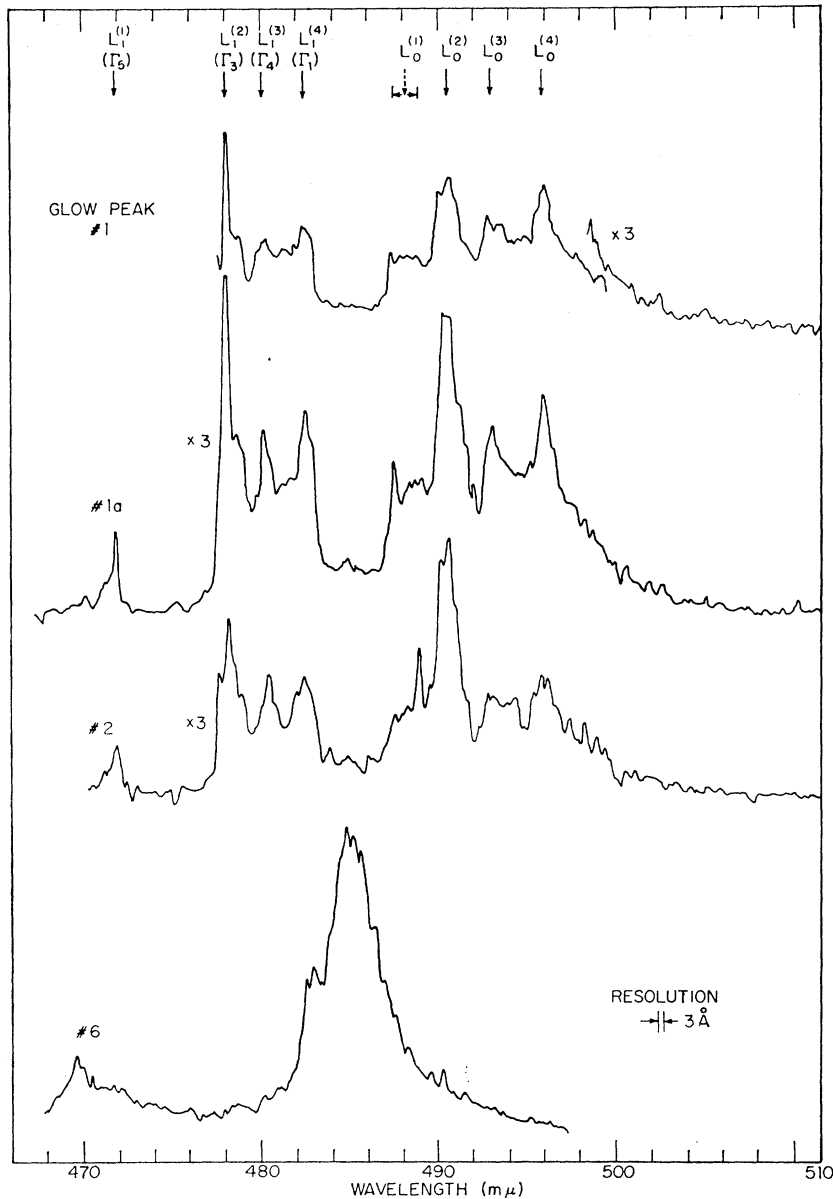


FIG. 2. Thermoluminescent spectra of 0.09% praseodymium. $L_0^{(i)}$ lines are transitions from 3P_0 to ground state; $L_1^{(i)}$ are transitions from 3P_1 .

electric) dipole transitions only between this and the Γ_4 level of the ground state. However, several lines are observed, denoted by $L_0^{(i)}$ in Fig. 2. The strongest of these occurs at 4905 Å, which may be the Γ_1 to Γ_4 transition. The other lines may be due to a partial breakdown in the selection rules because of mixing of higher states, or vibrational sidebands. Their energy spacing is approximately right for either of these possibilities, and the correct interpretation is still in doubt.

It is important to note that this cubic spectrum recurs for each of the measurable glow peaks below room temperature, while it changes radically above room temperature. The transitions from both the 3P_1 and 3P_0 states are shifted to higher energy for glow

peak No. 6. The lines are also broader, and the structure is washed out. This measurement is made above 400°K, since very little light is emitted between 160 and 400°K for praseodymium. The data do not warrant a more detailed analysis of the spectrum of this high-temperature glow peak.

C. Samarium

The thermoluminescent spectra of samarium could be recorded only for the two strong glow peaks, No. 1 and No. 2, for which identical results are obtained. Figure 3 compares this spectrum with the fluorescence at 77°K of another sample cut from the same boule of 0.1% samarium. Both of these recordings were obtained photographically.

More than 80 fluorescence lines for Sm^{3+} in the range from 6802 to 5583 Å have been listed by Rabbiner.¹¹ Of these, 29 lines are attributed to transitions from the ${}^4F_{5/2}$ state to the three lowest spin-orbit levels of the sextet H multiplet, all split by an axial crystal field. In the wavelength range covered by Fig. 3, two of these states are included: ${}^4F_{5/2}$ to ${}^6H_{7/2}$ and ${}^4F_{5/2}$ to the ${}^6H_{5/2}$ ground state. For these two sets of transitions, all of the lines listed by Rabbiner are seen except Nos. 68, 69, W71, W72, W75, and W76. (The numbering scheme used here is that of Rabbiner, where W or S means that the line is weak or strong. All the lines labeled in Fig. 3 are listed by Rabbiner as strong, except W63.) The lines which are seen in Fig. 3 agree with the wavelengths measured by Rabbiner to within a few angstroms. This agreement is felt to be good evidence that the fluorescence originates from ions in axial symmetry. The actual assignment of spectroscopic quantum numbers to these lines is suspect, however, since the Stark splittings are not small compared to the spin-orbit splittings.¹² Nevertheless, the large number of lines observed and the relatively good fit of these lines to a simple crystal-field theory with axial symmetry

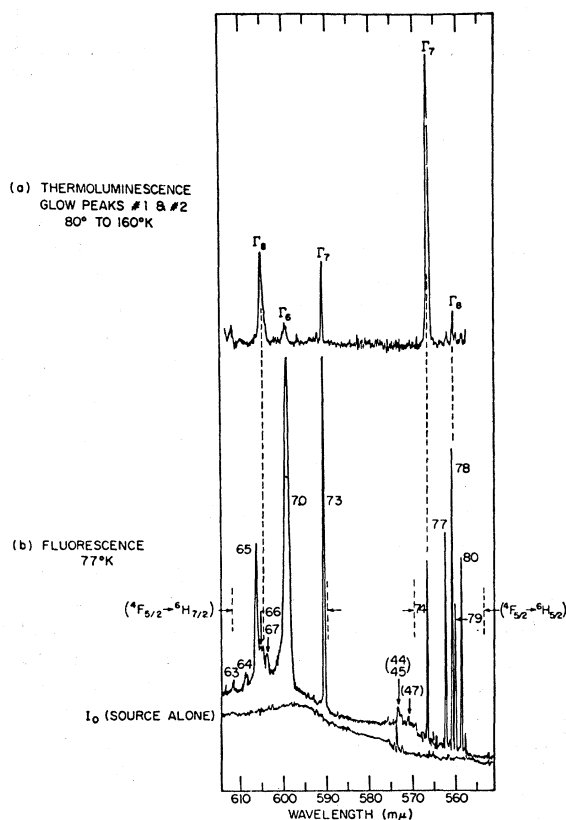


FIG. 3. Thermoluminescent and fluorescent spectra of 0.1% samarium. Fluorescent line numbers correspond to notation of Rabbiner (Ref. 11).

¹¹ N. Rabbiner, Phys. Rev. **130**, 502 (1963).

¹² N. Rabbiner, Phys. Rev. **132**, 224 (1963).

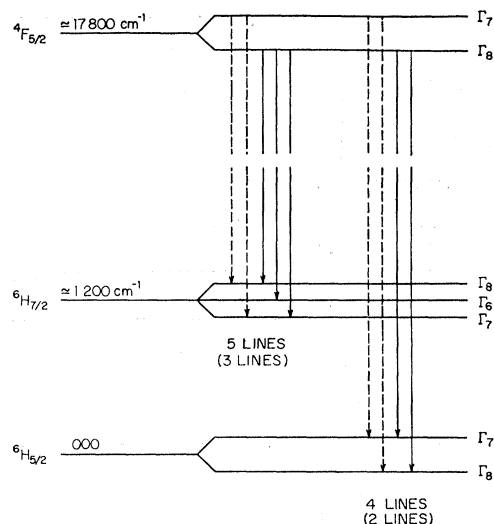


FIG. 4. Allowed dipole transitions for Sm^{3+} in a cubic field, between the ${}^4F_{5/2}$ and the ${}^6H_{7/2,5/2}$ states. The number of transitions is given in parentheses when only the Γ_8 level of the excited state is involved.

offer convincing proof that a lower symmetry than cubic is involved in the fluorescence data. The discussion of charge compensation in I suggests that the symmetry may be tetragonal, or that several different sites may contribute to the fluorescent spectrum of Fig. 3.

The transitions expected between these levels in a cubic field are shown in Fig. 4. Five transitions should be seen to the ${}^6H_{7/2}$ level and four to the ${}^6H_{5/2}$ ground state. However, for the trivalent rare earths in CaF_2 the spin-lattice relaxation times at the temperatures of interest are found to be quite fast, usually of the order of microseconds.¹³ One might therefore expect fluorescence only from the Γ_8 level of the ${}^4F_{5/2}$ state. If this were the case, the dashed lines in Fig. 4 would not be observed, and only three and two lines would result for transitions to ${}^6H_{7/2}$ and ${}^6H_{5/2}$, respectively. The thermoluminescent data in Fig. 3(a) actually shows such a three-line and two-line pattern, and the crystal-field components of the terminal states are tentatively identified as Γ_6 , Γ_7 , and Γ_8 . The three lines terminating at the ${}^6H_{7/2}$ level fit the splitting diagram of LLW for the value $x=0.94$, while Weber and Bierig¹⁰ estimate $x \approx 1$. The evidence again favors an interpretation of the low-temperature thermoluminescence as originating from ions in cubic sites.

D. Europium

Thermoluminescence from europium-doped samples was extremely difficult to observe, as discussed in I. Only in low resolution was any thermoluminescence detected: This was a broad band between 4200 and 4500 Å, peaking at about 4300 Å. The possibility that

¹³ R. W. Bierig, M. J. Weber, and S. I. Warsaw, Phys. Rev. **134**, A1504 (1964).

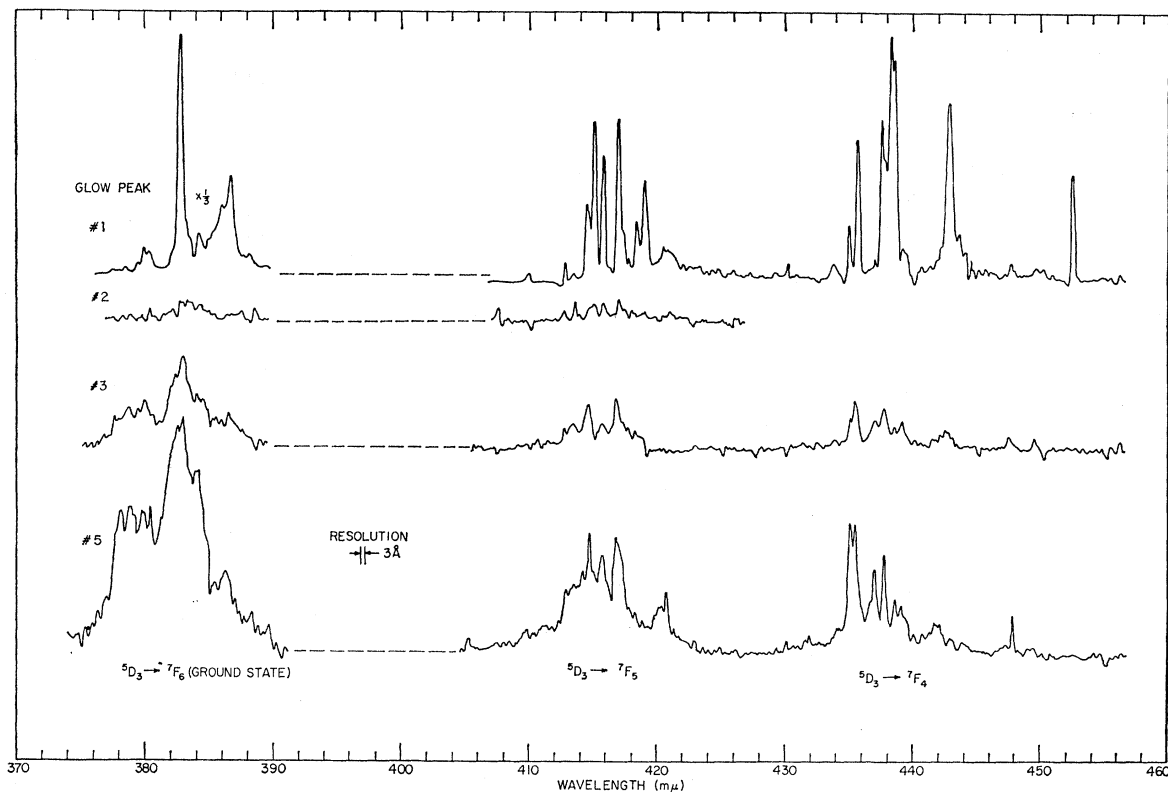


Fig. 5. Thermoluminescent spectra of 0.1% terbium.

this is associated with impurities or with a hole produced by irradiation has been mentioned; however, another possibility should be pointed out. The thermoluminescence of dilute europium is very similar to the fluorescence of Eu^{2+} at room temperature. A mechanism similar to that found for the other trivalent ions might therefore be operative for divalent europium: Irradiation produces a small fraction of Eu^{1+} ions, which are re-oxidized to the Eu^{2+} state when heated, emitting light in the form of Eu^{2+} fluorescence. Further experimental work is required to test this hypothesis,¹⁴ but such a mechanism would be consistent with the data presented here.

E. Terbium

Figure 5 shows the thermoluminescent spectra for 0.1% terbium. Emission is seen from the 5D_3 state to three of the spin-orbit states of the septet F multiplet, including the ground state 7F_6 . The resolution used for these traces is about 3 Å. In addition, emission was observed from the 5D_4 level in low resolution (not shown in Fig. 5). A satisfactory explanation for these spectra has not been found in terms of transitions in a field of cubic or lower symmetry. Complications such

¹⁴ To prove this emission originates from divalent europium, the thermoluminescent spectra should be measured near 100°K, where the broad Eu^{2+} fluorescence band splits into characteristic sharp lines, Cf. P. P. Feofilov, Opt. i Spektroskopiya 1, 992 (1956).

as vibrational sidebands or admixtures of states of different J may occur. Furthermore, a sharp distinction between high- and low-temperature glow peaks cannot be made. Instead, the spectra seem to gradually change character from glow peak No. 1 to peak No. 5. A general broadening with temperature is seen. These results are not understood in terms of the behavior of other ions studied, and the spectra await further experimental work for interpretation.

F. Dysprosium

Only a few strong lines were observed in the thermoluminescence of dysprosium, and these could be given a simple interpretation. The results are shown in Fig. 6, where comparison is made with fluorescence measurements on the same sample. The ground state of Dy^{3+} is ${}^6H_{15/2}$, which splits in a cubic field into Γ_6 and Γ_7 doublets and three Γ_8 quartets. The emission shown in this figure is from the ${}^6F_{11/2}$ state. The spacing of five of the lines observed from the low-temperature glow peaks fits the $J = 15/2$ splitting diagram given by LLW for $\alpha = 0.6$ with reasonable accuracy. A value of $\alpha = 0.59 \pm 0.01$ has been measured by Low.¹⁵ It appears, therefore, that the lines labeled Γ_i in the thermoluminescent spectra of dysprosium are transitions from the lowest level of the ${}^6F_{11/2}$ state to the ground state,

¹⁵ W. Low, Phys. Rev. 134, A1479 (1964).

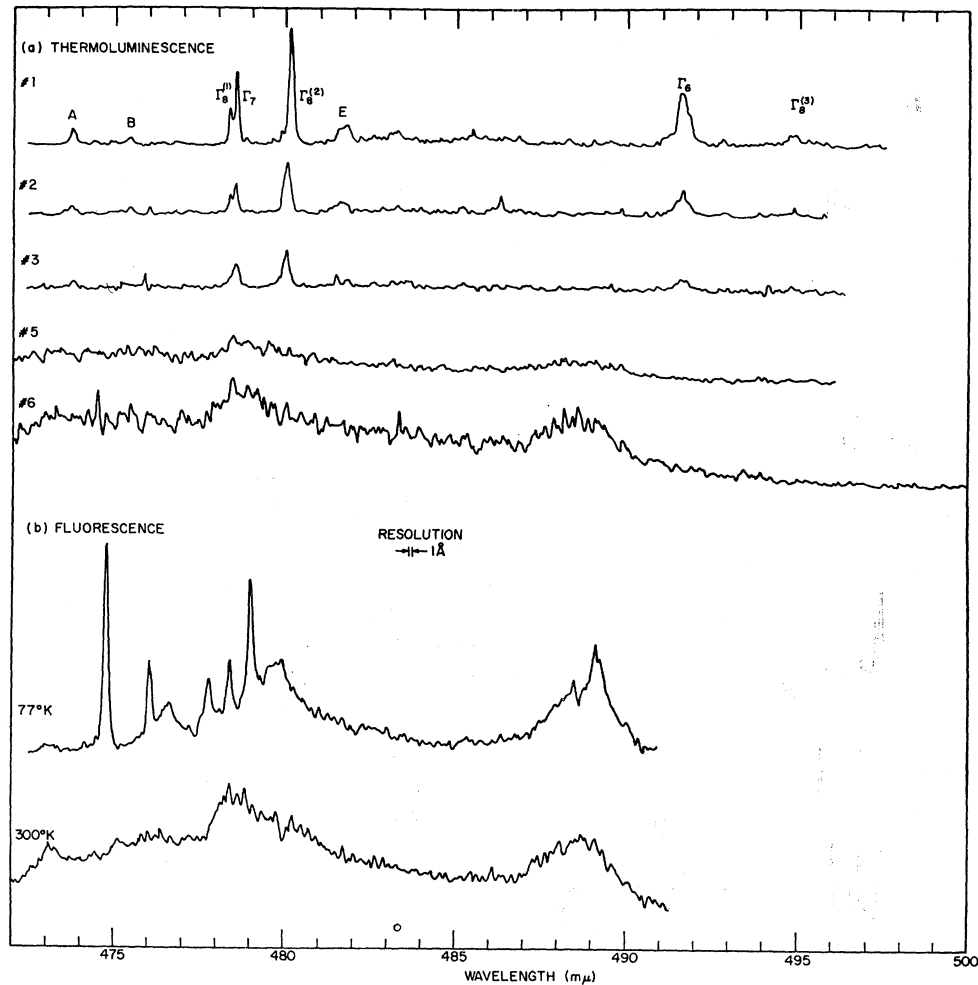


Fig. 6. Thermoluminescent and fluorescent spectra of 0.09% dysprosium. Γ_6 , Γ_7 , Γ_8 are cubic field levels of ${}^6H_{15/2}$ ground state. A is emission from an excited crystal-field level. B and E are believed to be vibrational lines (Ref. 16).

split by a cubic field. This has already been pointed out by Kiss and Staebler,¹⁶ who photographed all the light emitted from a sample of $\text{CaF}_2:\text{Dy}$ after γ irradiation at 78°K and warming to room temperature. The data in Fig. 6 separate the three glow peaks below room temperature, and the results for each glow peak are identical with those of Kiss and Staebler. These authors also identify the line labeled A as emission from one of the higher levels of the ${}^6F_{11/2}$ state, and suggest that the lines B and E may be vibronic components.

Comparison with the fluorescence of Dy^{3+} at 77°K is also made in Fig. 6. The Γ_8 quartets obviously split, and a more complicated spectrum results. This splitting requires a descent in symmetry from cubic, and tetragonal symmetry would be expected from charge compensation. These fluorescent data are also identical with the measurements of Kiss and Staebler.

¹⁶ Z. J. Kiss and D. L. Staebler, Phys. Rev. Letters 14, 691 (1965).

Spectral measurements at or above room temperature are inconclusive. The lines broaden considerably so that the symmetry of the emitting ion cannot be determined. The general shape of the fluorescence at 300°K resembles the low-temperature fluorescence, with all sharp-line structure washed out. The thermoluminescence from glow peaks Nos. 5 and 6 also has this same shape.

G. Erbium

The thermoluminescent spectra of 0.1% erbium was measured photographically. Densitometer traces are shown in Fig. 7. Traces (a) through (d) are the emission of glow peaks Nos. 1, 2, 3, and 5 in the range 5200–5700 Å. (Emission is too weak to be seen from the fourth glow peak.) Once again the emission from all of the glow peaks below room temperature (Nos. 1, 2, 3) is identical, differing only in intensity. The spectrum from the high-temperature peak (No. 5) is simpler than the emission below room temperature.

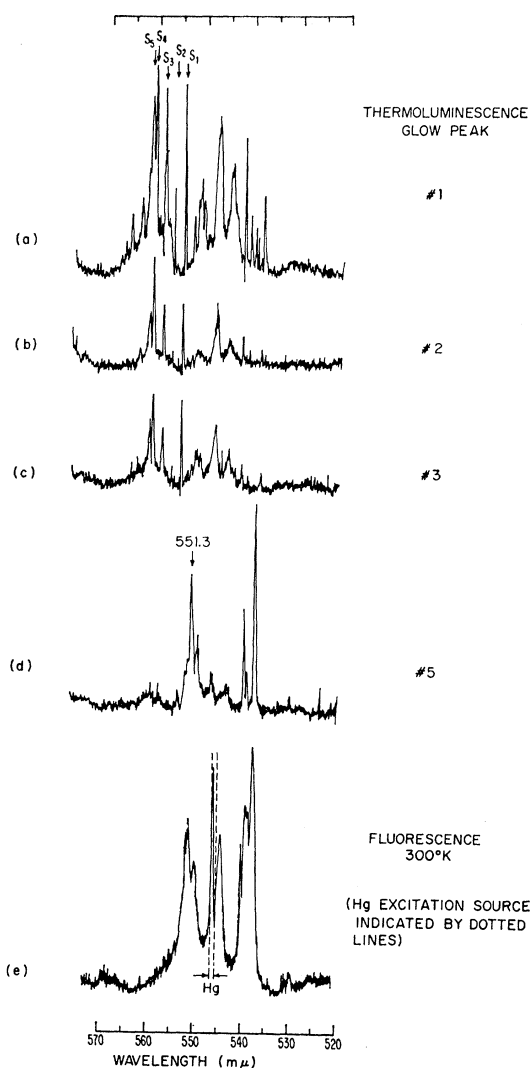


FIG. 7. Spectra of 0.1% erbium. (a) to (d): thermoluminescence of glow peaks Nos. 1, 2, 3, and 5 after irradiation. Vibrational sidebands of 5513 Å line denoted by S_1, \dots, S_5 . (e): fluorescence at 300°K.

This is unexpected, since the results for the other ions predict additional lines due to tetragonal distortion for peak No. 5. Comparison with trace (e) shows that the high-temperature glow emission is very similar to the fluorescence of Er^{3+} at room temperature, and the evidence strongly suggests that this spectrum is indeed due to tetragonal symmetry. Rector *et al.*¹⁷ have studied the Zeeman splitting of erbium fluorescence in CaF_2 , and found that emission from tetragonal sites dominated the optical spectra. Erbium fluorescence has also been measured with high resolution by Pollack.¹⁸ Traces (d) and (e) in Fig. 7 resemble the results of these investigators, and the symmetry associated with

¹⁷ C. W. Rector, B. C. Pandey, and H. W. Moos, *J. Chem. Phys.* **45**, 171 (1966).

¹⁸ S. A. Pollack, *J. Chem. Phys.* **40**, 2751 (1964).

these high-temperature cases is believed to be tetragonal.

A strong tetragonal line at approximately 5513 Å is found in glow peak No. 5, and is reported by Rector and by Pollack at 5512 Å. However, a series of lines on the low-energy side of this line shows up in the low-temperature glow peaks which is not reported in the fluorescence data. These lines are listed in Table I.

These extra lines seen in the low-temperature peaks are believed to result from the following mechanism. The transition responsible for these lines is from the $^4S_{3/2}$ state to the $^4I_{15/2}$ ground state. This transition involves $\Delta L = \Delta J = 6$, and is therefore strongly forbidden. In the operator equivalent expansion for a cubic-crystal field only the fourth power of the raising and lower operators appears, so that the transition is still forbidden in a cubic field, and the observed emission is probably vibronically induced. The line at 5513 Å, which is strong in the high-temperature glow peak (denoted by arrow), has vibronic sidebands (denoted by S_i) in the low-temperature peaks shifted to lower energy by 100, 160, 234, 304, and 323 cm^{-1} . Weaker lines can also be seen at 383 and 450 cm^{-1} . The ionic radius of Er^{3+} is close to that of the Ca^{2+} ion it replaces, and its mass is approximately four times greater. It might be expected that vibrational lines would appear at frequencies corresponding to peaks in the density of states for lattice vibrations in CaF_2 . These peaks occur at the critical points of the phonon dispersion curve. Comparison with the dispersion curves for CaF_2 given by Ganesan and Burstein¹⁹ shows that most of the additional lines pointed out in Fig. 7 occur near critical points. Only one observed sideband (100 cm^{-1}) does not correspond to a critical point. All the other sidebands have at least one mode with a critical point near the sideband frequency.

The explanation for the line at 100 cm^{-1} may involve a localized mode of the XY_8 complex surrounding the

TABLE I. Emission lines from $^4S_{3/2}$ to $^4I_{15/2}$ (in angstroms) for 0.1% erbium. Relative intensities given in parentheses as very strong (VS), strong (S), medium (M), weak (W), and very weak (VW).

Rector	Pollack	Glow peaks No. 1-No. 4	Shift from 5513 line (in cm^{-1})
5512.33 (S)	5512.3 (VS)	5513 (W)	
5522.12 (W)	5522.5 (M)	5521 (W)	
5526.80 (M)	5527.2 (S)	...	
	5545.8 (VW)	S_1 : 5544 (S)	100
	5561.4	S_2 : 5562 (M)	160
		S_3 : 5585 (S)	234
		S_4 : 5607 (S)	304
		S_5 : 5613 (S)	323
		5632 (W)	383
		5653 (W)	450

¹⁹ S. Ganesan and E. J. Burstein, *J. Phy. (Paris)* **26**, 645 (1965).

rare earth. The vibrational frequency is proportional to the inverse square root of the mass; since the erbium ion is approximately four times heavier than the Ca^{2+} ion, the reduction of a lattice mode frequency by a factor of 2 would be expected. Localized modes have been observed and identified in SrF_2 and SrCl_2 doped with Sm^{2+} by Axe and Sorokin²⁰ and in $\text{CaF}_2:\text{Dy}^{2+}$ by Kiss.²¹ For dysprosium, Kiss found a vibronic line at 100 cm^{-1} , as well as lines at 180, 270, and 400 cm^{-1} , which seemed to result from localized modes.

The thermoluminescent spectra for erbium are consistent with the results for gadolinium and other ions studied. For all of the peaks occurring below room temperature, the emission appears to be from ions in cubic sites, but because the transition is forbidden, only vibronic sidebands are seen. For the glow peaks above room temperature, the emission again seems to be characteristic of tetragonal symmetry.

H. Holmium

Thermoluminescence has been observed from the $^5\text{S}_2$ state to the $^5\text{I}_8$ ground state of Ho^{3+} . The transition is very similar to the emission seen for erbium, where $^4\text{S}_{3/2}$ and $^4\text{I}_{15/2}$ levels were involved. In both cases $\Delta J = \Delta L = 6$, and the upper multiplets lie at nearly the same energy for the two ions. The spectra for the two ions are in fact very similar, and the numerous lines seen for holmium are also believed to result from vibrational effects.

Seventeen lines have been measured photographically in the region from 5600 to 5365 Å for a 0.1% holmium sample. These are listed in Table II; the energies tabulated there are correct to within 10 cm^{-1} for each

TABLE II. Thermoluminescent^a spectrum of 0.1% holmium.

Line	λ (Å)	λ^{-1} (cm^{-1})	Holmium sidebands (cm^{-1})	Erbium sidebands ^b (cm^{-1})
1	5365	18 639		
2	5374	18 608		
3	5383	18 577		
4	5402	18 512		
5	5409	18 488		
6	5419	18 453	0	0(18 139 cm^{-1})
7	5428	18 423		
8	5449	18 352	101	100
9	5455	18 332		
10	5469	18 285	168	160
11	5479	18 252		
12	5486	18 228	225	234
13	5511	18 146	307	304
14	5514	18 136	317	323
15	5540	18 051	402	383
16	5568	17 960	493	450
17	5598	17 864		

^a Thermoluminescence photographed between 77 and 300°K. Energies correct to 10 cm^{-1} .

^b Values of erbium sidebands taken from Table I. The no-phonon line for erbium occurs at $5513\text{ Å} = 18\,139\text{ cm}^{-1}$.

²⁰ J. D. Axe and P. P. Sorokin, Phys. Rev. **130**, 945 (1963).

²¹ Z. J. Kiss, Phys. Rev. **137**, A1749 (1965).

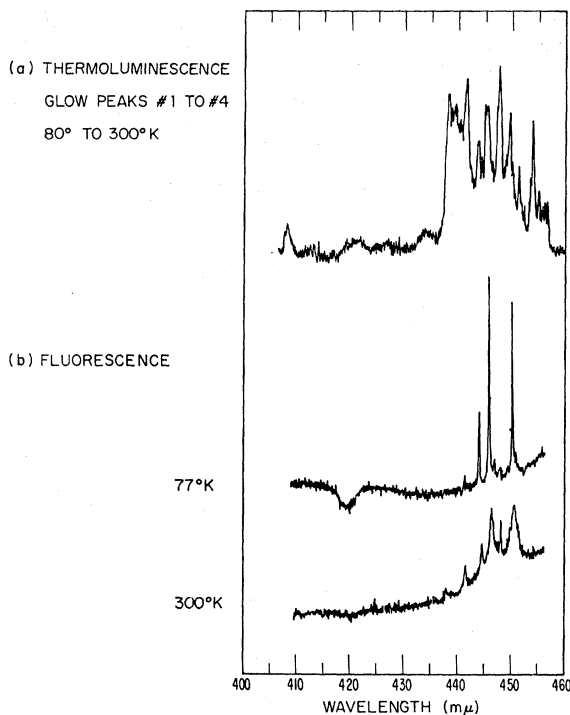


FIG. 8. Thermoluminescent and fluorescent spectra of 0.12% thulium.

line. A single exposure was made while the sample was heated from 77 to 300°K after irradiation; separation of the emission into each of the low-temperature glow peaks was therefore not achieved.

By shifting the spectrum 314 cm^{-1} to lower energy, a close similarity with the low-temperature spectrum of erbium becomes noticeable. If the weak Ho^{3+} line at 5419 Å (designated line 6 in Table II) is chosen as a parent line, then sidebands appear shifted to lower energy by 101, 168, 225, 307, 317, 402, and 493 cm^{-1} . These lines are remarkably similar to the erbium lines attributed to vibrational effects. Two additional lines, designated 9 and 11, are interspersed in this list of holmium sidebands. These may be overlapping sidebands associated with other crystal-field levels. Because of the higher degree of degeneracy of the holmium free-ion states, more transitions are expected for Ho^{3+} than for Er^{3+} .

I. Thulium

Both photographic and photoelectric methods were employed to study the spectra of thulium. A portion of the spectral range measured photographically is shown in Fig. 8; this corresponds to transitions from $^1\text{G}_4$ to the $^3\text{H}_6$ ground state. The fluorescence at room temperature, shown in part (b) of the figure, consists of six lines. Many more lines are seen in thermoluminescence between 77 and 300°K. Once again it is suggested that these are vibrational sidebands. The

transition involved here requires $\Delta L=1$ and $\Delta J=2$, which excludes a magnetic or electric dipole transition in a cubic crystal field. If the transition is electric dipole, then lattice vibrations would be required to remove the center of inversion.

Photoelectric measurements of the thermoluminescence showed that the spectrum in Fig. 8(a) was repeated identically for each of the peaks below room temperature. However, a new spectrum appeared for peaks Nos. 5 and 6, which had far more lines. Thus, the evidence again implies a descent in symmetry for the high-temperature thermoluminescence.

J. Lanthanum, Cerium, Neodymium, and Ytterbium

No sharp line structure is seen for lanthanum since La^{3+} has no $4f$ electrons. Instead, broad-band emission is seen. This is probably characteristic of unknown impurities, but discussion of this point will be postponed until the spectra from undoped crystals are considered.

Sharp emission lines are also absent for the case of cerium, since the f^1 configuration of Ce^{3+} has only a doublet F level. Spin-orbit coupling splits this doublet by approximately 2000 cm^{-1} . However, broad uv bands are observed which are believed to be transitions from the $5d$ configuration.^{22,23}

The thermoluminescence from neodymium is weak, so that only low-resolution spectral measurements could be made (resolution of about 15 \AA). The spectrum did not change very much for peaks Nos. 3, 5, and 6, but the resolution was not adequate for crystal-field determinations. The emission from glow peaks Nos. 1, 1b, and 2 was too weak even for low-resolution measurements.

No spectral measurements were made for ytterbium, since the only excited state is in the infrared, at about $1\text{ }\mu$. However, these measurements would be useful, since the transition would involve only $J=\frac{5}{2}$ and $J=\frac{7}{2}$ multiplets, and the spectra should therefore be easy to interpret.

K. Oxygen-Compensated Erbium

The effect of oxygen compensation on the integrated glow curve of erbium was discussed in I. The thermoluminescence was strongly quenched by doping with Er_2O_3 instead of ErF_3 , and only a single glow peak at 130°K was observed. It is also of interest to examine the spectrum of this glow peak. Photoelectric measurement of the emission from this peak gave a spectrum similar to the type-I fluorescence identified by Stepanov and Feofilov,²⁴ associated with charge compensation by

²² A. A. Kaplyanskii, V. N. Medvedev, and P. P. Feofilov, *Opt. i Spektroskopiya* **14**, 664 (1963) [English transl.: *Opt. Spectry. (USSR)* **14**, 351 (1963)].

²³ E. Loh, *Phys. Rev.* **147**, 332 (1966).

²⁴ I. V. Stepanov and P. P. Feofilov, *Dokl. Akad. Nauk. SSSR* **108**, 615 (1957) [English transl.: *Soviet Phys.—Doklady* **1**, 350 (1956)].

substitutional O^{2-} ions at lattice fluoride sites. A similar spectrum was seen in fluorescence for the Er_2O_3 -doped sample. The absence of these dominant effects on the glow curves and spectra of trifluoride-doped crystals is convincing evidence that very little oxygen is present, and that the phenomena studied in this work are related to fluoride compensators.

L. Undoped CaF_2

The existence of weak, broad emission bands in both doped and undoped crystals of CaF_2 has been mentioned several times; the thermoluminescence of La, Pr, Eu, Cd, and undoped samples exhibited such bands. The photoelectric detection scheme was also used to study the emission from individual glow peaks of an undoped crystal grown from G&S CaF_2 ; results are shown in Fig. 9. The low-temperature and high-temperature glow peaks have different spectra, while the intermediate peaks (Nos. 4 and 4a) show both types. A similar behavior was observed for the La-doped sample, except that peak No. 5 resembled the low-temperature peaks. The undoped sample was grown in the crystal furnace simultaneously with three erbium-doped samples; consequently, a slight contamination with erbium would not be surprising, and is in fact observed in the highest temperature glow peak in Fig. 9.

Two possible explanations for these broad bands have been suggested earlier. The first is simply the presence of trace amounts of impurities. Since the rare earths are difficult to separate, several rare earths may be present. La, Ce, and Eu are all possibilities, although it is difficult to explain the shift of the emission band by 6500 cm^{-1} for different glow peaks using such a model. The characteristic sharp-line spectra of the other rare earths disclose their presence.

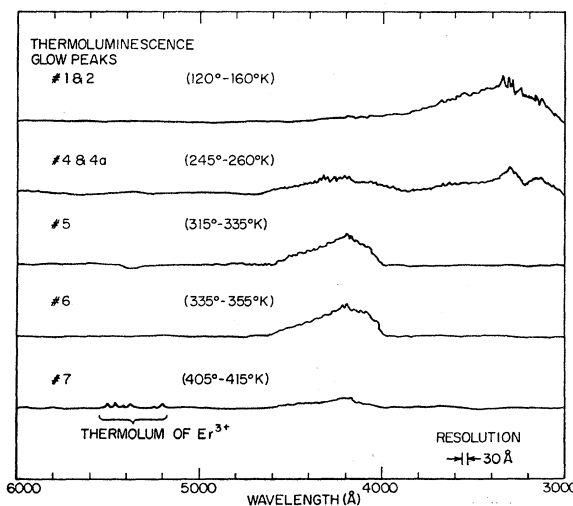


FIG. 9. Thermoluminescent spectra of undoped CaF_2 . Grown from G&S powder.

Yttrium is another common contaminant in these crystals. O'Connor and Chen⁴ found that yttrium was responsible for absorption bands in CaF_2 previously attributed to color centers. A very broad emission band was observed from a Y-doped sample throughout the ultraviolet, but the spectrum was not similar to that obtained for undoped crystals. Other impurities are also possible, and an attempt was made to isolate them by studying crystals grown from different sources of CaF_2 . The results of these experiments were inconclusive, however; in some cases similar spectra were obtained from samples whose integrated glow curves were significantly different, while other undoped samples displayed somewhat different spectra.

This broad-band luminescence might instead be emitted by the radiation-produced hole centers during recombination with the trapped electrons. An absorption band has been found which could be associated with these holes, and it is not unreasonable to expect characteristic luminescence from these centers as well. Differences in the spectra of various undoped samples might then result from slightly different configurations of the centers which are favored in each sample.

IV. DISCUSSION OF RESULTS

A definite pattern can be discerned from the spectral data presented above. For all of the glow peaks occurring below room temperature, the emission originates from an ion in a cubic site, while the high-temperature glow peaks display a lower symmetry which is believed to be tetragonal. This is best seen in the spectra of Gd, where the fluorescent spectrum has been identified for each type of charge compensator. Cubic emission below room temperature is also seen for Pr and Dy, and probably for Sm. Evidence for vibrationally assisted transitions in cubic symmetry is given for Er, Ho, and Tm. For most of these ions additional lines appear in the glow peaks above room temperature, indicating a descent in symmetry from cubic. In some cases this can be identified as tetragonal. The ions La, Ce, and Yb do not have sharp line structure in the region of these measurements, so crystal-field analysis is impossible. The emission from Nd is too weak for study, while Eu is already reduced in the lattice and therefore emits very little light. This leaves only Tb, whose complicated spectra could not be properly analyzed.

The important result of this paper is therefore the accumulation of evidence that the low-temperature glow peaks are characteristic of ions in cubic sites, while the large peak above room temperature is tetragonal. The similarity of the spectra for the low-temperature glow peaks has been made more convincing by an interferometer experiment, where the sharp Er line at 5544 \AA (denoted by S_1 in Fig. 7) was monitored using the higher resolution attainable with a Fabry-Perot etalon. (This experiment is described in detail

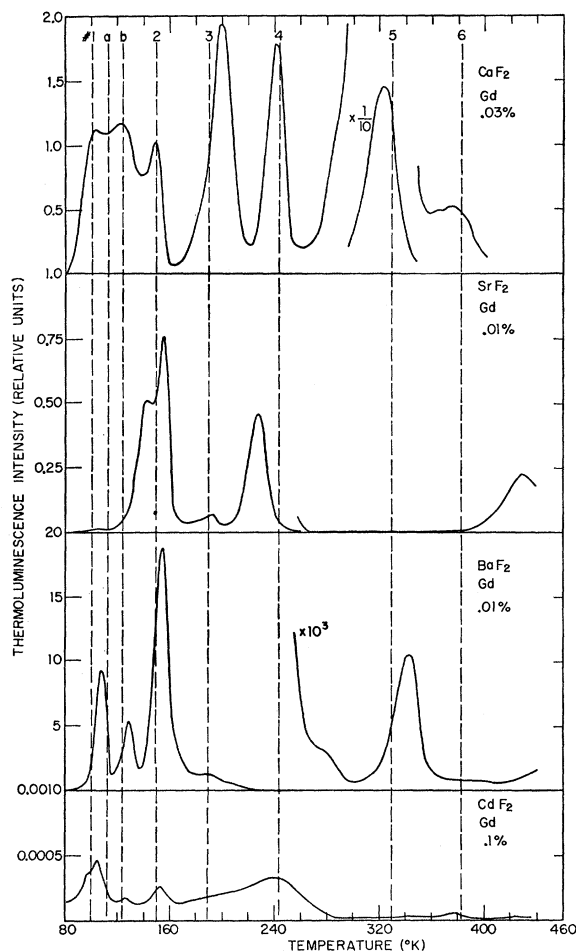


FIG. 10. Thermoluminescent glow curves of the alkaline earth fluorides doped with gadolinium.

in Ref. 25.) No shift greater than 1 cm^{-1} was detected for the first three glow peaks. These results are in sharp disagreement with the explanation offered by O'Connor⁵ for the thermoluminescence observed from $\text{CaF}_2 \cdot \text{Y}$. In the latter case the series of emission lines observed are attributed to radiative recombination of highly associated Y^{2+} -hole pairs; each different pair separation produces an emission line at a different energy. No evidence of this sort of mechanism is found for the rare earths. Even in the undoped and Y-doped crystals, the thermoluminescence is not the same as the spectra reported by O'Connor. However, the results reported in this paper were obtained at much lower irradiation doses.

The nature of the thermoluminescence observed from undoped crystals has not been definitely identified in

²⁵ J. L. Merz, Ph. D. thesis, Harvard University, 1966 (unpublished). Available as Technical Report No. 514, Office of Naval Research, NR-372-012.

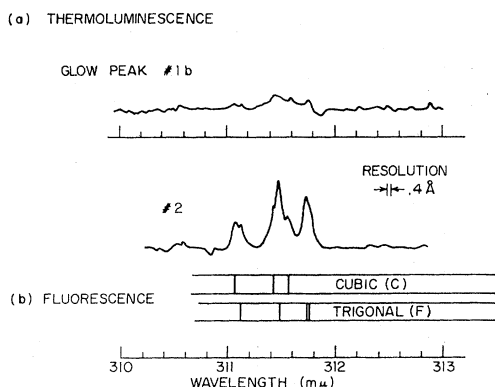


FIG. 11. Thermoluminescent spectra of $\text{SrF}_2:\text{Gd}$ 0.01%. Fluorescent data in bar graphs from Makovsky (Refs. 7, 28) (see text).

this work. The emission could originate from impurities in the crystals, or could result from the recombination of electrons and holes. The former situation is undesirable and could presumably be eliminated by increasing the purity of the crystals. The latter mechanism is much more interesting. If this emission is actually recombination radiation, then spectral data such as that presented here could provide additional information about the hole centers involved. Luminescence of this type has been observed for V_K centers in the alkali halides.^{26,27} It should be emphasized that in rare-earth-doped crystals these effects are dominated by the intense emission of the impurity ion.

V. GADOLINIUM IN SrF_2 , BaF_2 , AND CdF_2

The glow curves of gadolinium in the hosts CaF_2 , SrF_2 , BaF_2 , and CdF_2 are shown in Fig. 10. The $\text{CaF}_2:\text{Gd}$ curve is reproduced from I, Fig. 1, where all the rare-earth ions were studied in CaF_2 . The most obvious difference between the behavior of CaF_2 and its isomorphs is the suppression of glow peak No. 5. This suppression is greatest for the barium crystal. The only glow peak which appears consistently is peak No. 2, which has been associated with the diffusion and recombination of V_K centers. A slight dependence on host lattice is also observed in this figure. Very little thermoluminescence is seen for $\text{CdF}_2:\text{Gd}$, shown on an expanded scale.

Because the emission is weak only the spectrum for glow peak No. 2 can be identified for SrF_2 ; it is shown in Fig. 11. For the BaF_2 spectra in Fig. 12, emission is also seen from peaks Nos. 1 and 1b, which are similar to the spectrum of peak No. 2. The spectral slit width for these measurements is 0.4 Å, corresponding to a resolution of $\approx 4 \text{ cm}^{-1}$.

The fluorescent spectra of Gd in cubic and trigonal

sites in these hosts are also indicated in Figs. 11 and 12. These were drawn by estimating the proper fit to the thermoluminescent spectra, with the aid of spectrograms published by Makovsky⁷ for the cubic fluorescence of Gd. In a later work,²⁸ Makovsky lists the energies of these lines; the agreement with the spectra of Figs. 11 and 12 is within the accuracy of these measurements (4 cm^{-1}).

Comparison of the spectra in these figures shows that Gd ions in both cubic and trigonal sites are contributing to the thermoluminescence at low temperatures. These results are not surprising in the light of the fluorescence and EPR experiments done on SrF_2 and BaF_2 . In the optical spectra, trigonal symmetry is strong in SrF_2 and dominates the emission in BaF_2 . Emission from sites of tetragonal symmetry is very weak. Similarly, the EPR spectra measured for Gd^{3+} and Ho^{3+} display trigonal symmetry. Evidently, the method of charge compensation for the trivalent rare earth in these hosts differs from that in CaF_2 . Compensation by interstitial F^- ions in the adjacent body-center position (leading to tetragonal symmetry) appears to be less favorable, and some mechanism producing trigonal symmetry becomes important instead. There are two possible causes for this trigonal symmetry: (1) the presence of interstitial fluoride compensators at the next-nearest-neighbor position [i.e. the empty cube center located along the (111) direction from the trivalent rare earth], and (2) the larger lattice spacing in SrF_2 and BaF_2 , allowing the rare earth to move away from the center of the cube toward one of the eight lattice F^- ions surrounding it.

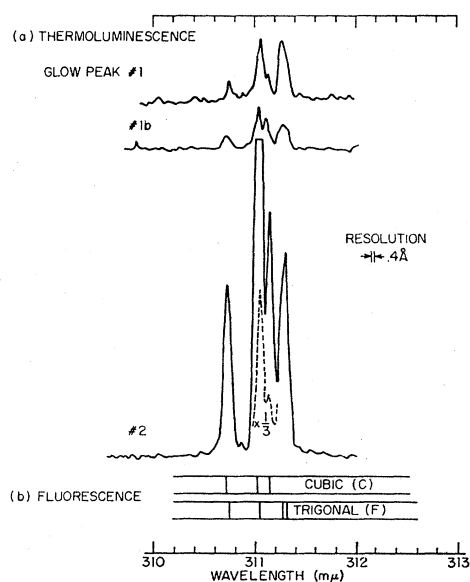


FIG. 12. Thermoluminescent spectra of $\text{BaF}_2:\text{Gd}$ 0.01%. Fluorescent data in bar graphs from Makovsky (Refs. 7, 28) (see text).

²⁶ M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

²⁷ R. B. Murray and F. J. Keller, Phys. Rev. **153**, 993 (1967).

²⁸ J. Makovsky, J. Chem. Phys. **46**, 390 (1967).

The case of CdF_2 is obviously different. Little thermoluminescence is observed. In general, this crystal exhibits an entirely different behavior than CaF_2 and its isomorphs. Trivalent rare earths in CdF_2 cannot be reduced to the divalent state by chemical baking; instead, the crystal displays the properties of a semiconductor when doped with several of the rare earths.²⁹

²⁹ P. F. Weller, *Inorg. Chem.* **4**, 1545 (1965).

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Effect of Paramagnetic Impurity on the Long Lifetime of Positron in Liquid Ammonia

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We have computed the paramagnetic quenching effect of lithium and sodium in liquid ammonia on the long-lifetime component of positron annihilation. The triplet-to-singlet conversion cross sections, calculated in the Born approximation, turn out to be $5.9 \times 10^{-14} \text{ cm}^2$ for Li and $7.2 \times 10^{-14} \text{ cm}^2$ for Na for thermalized positronium. Reasonable agreement with the meagre existing experimental data is obtained.

I. INTRODUCTION

IT has been known for quite some time that the two-quantum annihilation spectra of positrons in many liquids and gases show a long-lived τ_2 component and that this lifetime is affected appreciably by the presence of paramagnetic impurities.¹ Any process whereby the two-photon annihilation replaces the longer-lived three-photon annihilation and contributes to the τ_2 component is called quenching. Heynman, Osman, Veit, and Williams² discuss various types of processes involved—unpaired-electron exchange, angular-momentum reorientation, chemical-compound formation, pickoff, and spin reversal. The explanation of paramagnetic quenching is as follows: Orthopositronium (triplet) is formed first and is subsequently converted by electron-exchange collisions in the medium to the parapositronium (singlet), which then decays promptly. The paramagnetic impurity introduced into the medium provides extra electrons that can be exchanged easily with the electron in positronium. Since the latter does not have magnetic moment in either of the two states involved, magnetic forces can be neglected. It has been emphasized by Ferrell³ that the naive interpretation of the triplet to singlet conversion as a “spin-flip” process of the paramagnetic impurity is not correct. Rather one must consider the

electron exchange arising essentially from the anti-symmetrization requirements on the wave function of a many-electron problem.

A direct first-principle calculation of τ_2 embracing all aspects of the quenching would be difficult. However, the modification of τ_2 by a small concentration of paramagnetic impurities would be easier to compute, particularly when the scatterers are isolated. A theoretical calculation of the triplet to singlet conversion in collisions of orthopositronium with atomic hydrogen was given by Massey and Mohr,⁴ using the Born approximation. A more detailed calculation for the same system was given by Fraser⁵ who found that the Born approximation result was too high, as one would have expected, and that the cross section fell off rapidly with energy on the scale of electron volts. On the experimental side, positron annihilation in atomic hydrogen has not been studied so far. Other quenching agents such as oxygen and nitric oxide, or diphenylpicrylhydrazyl (DPPH) in liquid benzene require a calculation of scattering from complex molecules. Obviously, one would like to have a system sufficiently simple and hydrogenlike where calculations can be attempted and meaningfully compared with experiments; such a situation prevails in the study of positron annihilation in solutions of lithium and sodium in ammonia.⁶

¹ See for earlier work the review article by M. Deutsch and S. Berko, in *Alpha-, Beta-, and Gamma-Ray Spectroscopy*, edited by K. Sieghahn (North-Holland Publishing Company, Amsterdam, 1965), Vol. 2, p. 1583.

² F. F. Heynman, P. Osman, J. J. Veit, and W. F. Williams, *Proc. Phys. Soc. (London)* **78**, 1038 (1961).

³ R. Ferrell, *Phys. Rev.* **110**, 1355 (1958).

⁴ H. S. W. Massey and C. B. O. Mohr, *Proc. Phys. Soc. (London)* **A67**, 695 (1954).

⁵ P. A. Fraser, *Proc. Phys. Soc. (London)* **79**, 721 (1961).

⁶ See T. P. Das [in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1962), Vol. 4, p. 303] for an account of their properties.