Optical Study of CaF_2:Ho^{+3}[†]

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The spectral distribution of the thermoluminescent glow peaks at 155, 206, and 333°K and the room-temperature phosphorescence have been measured in CaF_2:Ho^{+3} following x irradiation. The emission comprises about sixteen lines between 5300 and 5600 Å, which arise from Ho^{3+} in sites of different symmetries. The relative intensities of groups of these lines change from peak to peak, which suggests that the compensator associated with the Ho^{+3} ion becomes mobile at about room temperature.

I. INTRODUCTION

IT is currently accepted that rare-earth ions enter the CaF_2 matrix substitutionally for Ca^{+2}. The rare earth is, however, more stable in the +3 state, so that charge compensation is required. A number of compensating mechanisms have been observed, which differ from each other in their local symmetries.[1]

The crystal-field splittings of the energy levels associated with the optical emission depend on the symmetry surrounding the emitting rare-earth ion. The present work is concerned with the optical emission of CaF_2:Ho^{+3}. Merz and Pershan[2] have included this system in their papers pertaining to thermoluminescence in rare-earth–doped CaF_2. In their work they presented a table of the emission lines they observed exposing a photographic plate in the spectrograph to the *total* emission between liquid-nitrogen temperature (LNT) and room temperature (RT). In the present work we were able to record the emission spectrum of the individual glow peaks between LNT and 350°K. The relative intensities of the various emission lines change from peak to peak in a way which, we suggest, may be an indication that the compensator associated with the Ho^{+3} ion becomes mobile at about room temperature. We have also studied the room-temperature phosphorescence and compared its spectral composition to that of the thermoluminescence.

II. EXPERIMENTAL

The crystals used in the present work were grown and supplied by the Harshaw Chemical Co. They were grown by adding HoF$_3$ to pure CaF_2 in the melt. The concentration of Ho^{+3} ions in the crystals is about 0.5%.

Cleaved crystals of about 8×5×1 mm were x-irradiated inside a vacuum cryostat with fused silica windows, typically for 30 min at LNT. The x-ray tube

had a copper anode and was operated at 20 kVp, 10 mA. The general glow curve and its spectral composition were taken simultaneously in the following way. A photomultiplier, RCA type 1P28, was placed at one window of the cryostat to allow the total glow to be recorded. The photocurrent from this photomultiplier was fed to a Keithley type 410 micromicro-ammeter, the output of which was recorded by a Varian type G-28 chart recorder. The opposite window of the cryostat was brought as close as possible to the entrance slit of a grating spectrograph, with f number about 2 and resolution of better than 3 Å. This spectrograph was designed and built by Dr. H. I. S. Ferguson of the Department of Physics, University of Western Ontario. Between glow peaks the photographic film was moved so that the spectral composition of each peak was recorded separately. The heating rate in these measurements was constant and was equal to 11°/min.

The room-temperature phosphorescence was obtained after x-irradiating the crystal at RT, typically for 1 h. The time-dependent decay and spectral composition were recorded with the sample sandwiched between the photomultiplier and the entrance slit of the spectrograph.

III. RESULTS

The general glow curve of CaF_2:Ho^{+3} in the temperature range 77 to 350°K is shown in Fig. 1. The crystal was x-irradiated for 30 min at LNT. Thermal activation energies for some glow peaks are given in Table I. These were calculated by the formula[3]

$$E = kT_g^2/\delta,$$

where E is the activation energy, k is Boltzmann's constant, T_g is the temperature of the glow-peak maximum, and δ is the high-temperature half-width of the glow peak ($\delta = T_2 - T_g$, where T_2 is the temperature at half-intensity on the high-temperature side of the peak).

Figure 2(a), 2(b), and 2(c) show the spectral distribution of the emission from peaks (A), (B), and (C),

[1] M. Schlesinger and P. W. Whippey, Phys. Rev. **171**, 361 (1968).
[2] J. L. Merz and P. S. Pershan, Phys. Rev. **162**, 217 (1967); **162**, 235 (1967).
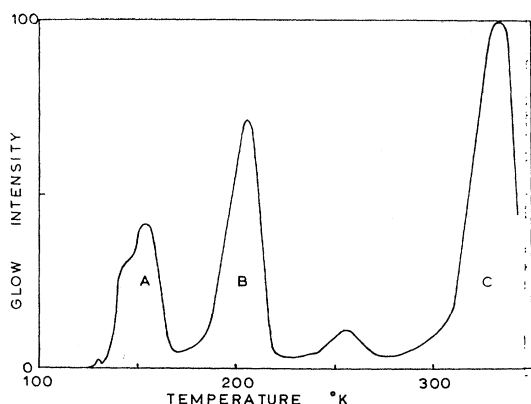[3] A. Halperin and A. A. Braner, Phys. Rev. **117**, 408 (1960).

FIG. 1. General glow curve of CaF_2:Ho^{+3} x-irradiated for 30 min at 77°K with heating rate of 11°K per min.

respectively, in Fig. 1. Note that the spectrum of peak (C) consists of less lines, about 10, than either peak (A) or (B), about 16. This difference will be discussed in Sec. IV.

Figure 3 is a log(intensity)-versus-log(time) representation of the decay of the room-temperature phosphorescence obtained after x irradiation (for 1 h) at room temperature. Figure 4 shows the spectral distribution of the room temperature phosphorescence. In Table II, a summary is given of the wavelengths of the different emission lines occurring in the various glow peaks as well as those occurring in the RT phosphorescence.

IV. ANALYSIS OF RESULTS AND DISCUSSION

A. Mechanism of Thermoluminescence

The electron configuration of Ho^{+3} is $4f^{10}$ with a ground state $^5I_8$. An excited state $^5S_2$ exists in the free ion at 1.83×10^4 cm^{-1} above the ground state which corresponds to the observed group of lines.

We assume the following mechanism for the thermoluminescent emission.[1,4] The ionizing radiation reduces some of the Ho^{+3} to the Ho^{+2} state. The hole created is trapped at a nearby site. Several types of trapping sites, corresponding to the different glow peaks, exist in the lattice. Upon heating, the trapped hole is released and recombines with the extra electron on the rare-earth ion, reoxidizing it to an excited $+3$ state. The

TABLE I. Activation energies of thermoluminescent peaks in CaF_2:Ho^{+3}.

Peak (see Fig. 1)	Temperature (°K)	Activation energy (eV). Error is ±10%
A	155	0.30
B	206	0.52
	256	0.62
C	333	0.95

[4] M. Schlesinger and P. W. Whippey, Phys. Rev. **162**, 286 (1967).

rare-earth $+3$ ion relaxes to its ground state, emitting its characteristic radiation. Hence, one expects the thermoluminescent emission to be characteristic of transitions within the rare-earth $+3$ ion.

B. Trapping Sites and Luminescence Centers

The model for the thermoluminescence described in Subsec. IV A requires that the luminescence centers and trapping sites exist as separate entities in the crystal;
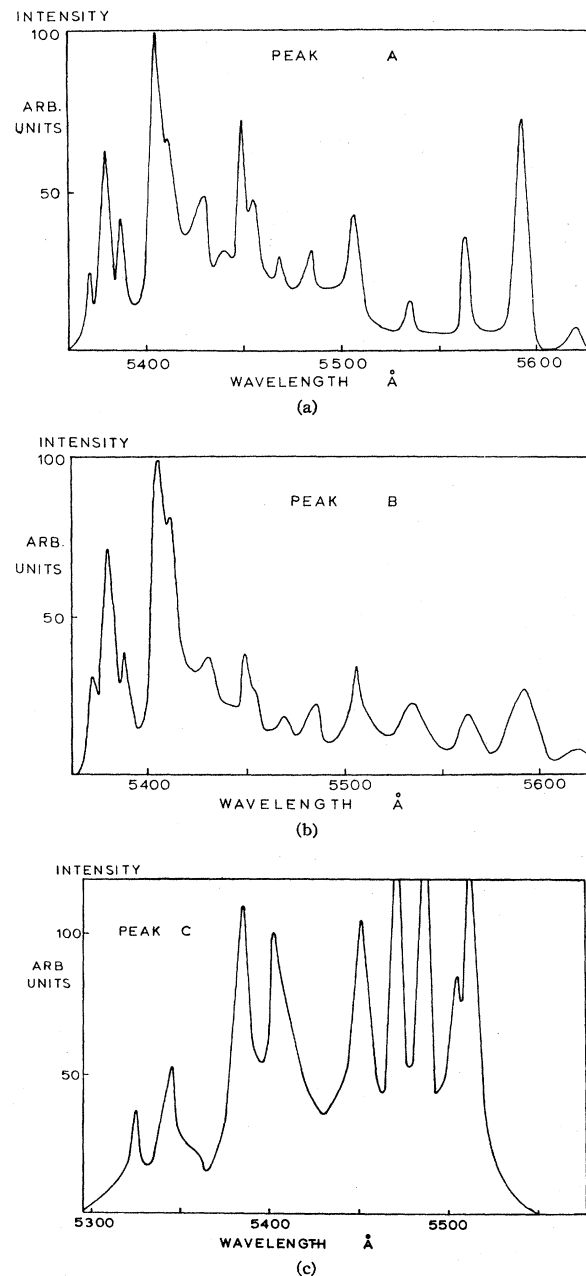

FIG. 2. Plot of the spectral composition of (a) the glow peak at 155°K (peak A, Fig. 1), (b) the glow peak at 206°K (peak B, Fig. 1), (c) the glow peak at 333°K (peak C, Fig. 1).
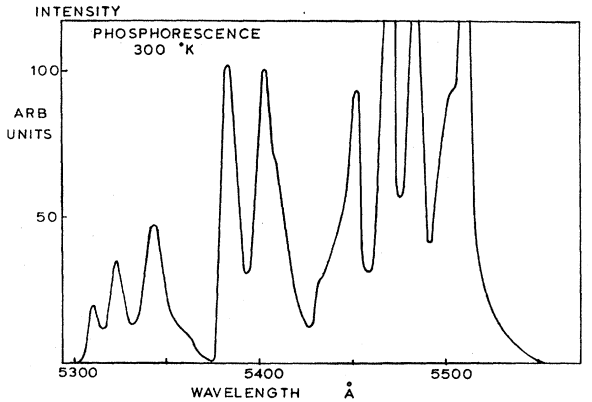
FIG. 3. Room-temperature phosphorescence decay of CaF₂:Ho⁺³ on a log (intensity)-versus-log (time) scale.

TABLE II. Wavelengths (Å) of the different emission lines in various glow peaks and room-temperature phosphorescence in CaF₂:Ho⁺³.

Peak A 155°K	Peak B 206°K	Peak C 333°K	Phosphorescence 300°K
			5308
		5320	5320
		5340	5339
		5350	5350
5371	5371		
5380	5380	5379	5379
5387	5387		
5405	5407	5396	5402
5411	5410		
5429	5430		
5440			
5449	5449	5446	5448
5453	5458		
5468	5469	5465	5465
5485	5486	5481	5481
		5498	5497
5507	5510	5504	5505
5534	5534		
5563	5562		
5591	5592		
5620	5620		

the luminescence centers comprise the rare-earth ions in the +2 state while the trapping sites are formed in the host lattice. Table III, compiled from results reported in this paper and Refs. 1 and 4, shows, however, that the glow peaks in CaF₂ doped with different rare earths do not occur at identical temperatures, so that the trapping sites are not characteristic solely of the host lattice. We suggest that the trapping sites are formed in the host lattice close to the rare-earth ion, and that this proximity causes changes in T_g, i.e., in the activation energies of the traps. Some evidence to support this is provided by the phosphorescence decay at constant temperature, Fig. 3, which shows a point of inflexion. The rate equations of phosphorescence decay have been considered by Adirowitch.[5] In this case, since there is one major thermoluminescent peak in CaF₂:Ho⁺³ above room temperature, we may consider the case where traps with a single mean lifetime are present, but where the capture cross section of empty luminescent centers, a_c, is presumably

different from the capture cross section of an empty trap, a_t (i.e., they exist as separate entities). A rigorous solution of the rate equations is not possible, but Adirowitch has given an approximate solution for equilibrium conditions and has also shown that a graph of log intensity as a function of log time has an inflexion, as is observed in Fig. 3, and that there is a range over which the luminescence intensity I follows an expression of the type

$$I = \text{const}/(t+t_0)^p.$$

From the value of p it is possible to infer the ratio

$$\frac{a_t}{a_c} = \frac{\text{capture cross section of traps}}{\text{capture cross section of luminescence centers}}.$$

In our present case we get an approximate value for this ratio of $\frac{1}{4}$.

C. Spectral Distribution

Comparison of columns 1 and 3 in Table II shows that the spectrum of the high-temperature peak at
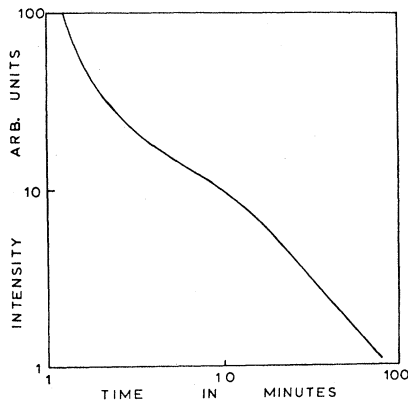

FIG. 4. Plot of the densitometer trace of the spectral composition of the room-temperature phosphorescence after x irradiation at room temperature for 60 min.

TABLE III. Glow-peak maxima T_g (°K) for Harshaw CaF₂ doped with different rare-earth ions [see present paper and Refs. (1) and (4)]. The same heating rate of 11 deg/min was used in all cases.

CaF₂:Ce⁺³	CaF₂:Gd⁺³	CaF₂:Ho⁺³
117		
	≈130	
	143	140
170	170	155
	≈220	206
	240	
		256
280	270	
		333

[5] For references see, for example, D. Curie, *Luminescence in Crystals*, translated by G. F. J. Garlick (Methuen and Company, Ltd., London, 1960).

333°K has only ten emission lines, while the peak at 155°K has sixteen lines. This suggests that the symmetry of the rare-earth ion sites associated with the 333°K peak is higher, e.g., cubic, than those sites associated with the 155°K peak. This may occur in the following way: After the reduction of the rare-earth ion to the $+2$ state, the compensator is no longer required. At about room temperature, it becomes mobile, leaving the Ho^{+2} in a cubic environment; on further heating, the hole is released from its trap and reoxidizes the Ho^{+2} to an excited Ho^{+3} in a cubic site; thus one expects the emission above RT to be characteristic of Ho^{+3} in a cubic site, the spectrum at low temperatures indicating the lower point symmetry surrounding the rare-earth ion. The possibility that the compensating ion is only weakly bound, and therefore relatively mobile, was recognized by Low and Ranon[6] in a discussion of their ESR measurements of CaF_2: Tm. Hayes et al.[7] have carried out ESR measurements at 4°K on CaF_2: Ho after x irradiation at room temperature. The Ho^{+3} ion is diamagnetic, but after irradiation had reduced some of the ions they observed a resonance due to Ho^{+2} in cubic sites only. Hayes et al.[7] may well have observed Ho^{+2} in cubic site only, because after x irradiation at room temperature had reduced the Ho^{+3} to Ho^{+2}, the compensator which is no longer required for local charge compensation, became mobile, leaving the Ho^{+2} ion in a cubic site even if originally it was in a site of lower symmetry. Merz and Pershan,[2] while not denying the possibility that the compensator may become mobile, at a relatively low temperature, favor a different approach. They propose that all thermoluminescent emission in rare-earth–doped CaF_2 below RT comes from ions in cubic lattice sites. For CaF_2: Er^{+3} whose spectrum shows similar tendency to the one observed here for CaF_2: Ho^{+3}, they suggest that the extra lines observed below room temperature are vibronically induced transitions, since the emission involves a transition where $\Delta L = \Delta J = 6$, which is forbidden in the free ion, and remains so in the cubic field. The present authors, however, have shown that, at least in the case of CaF_2: Gd^{+3},[4,8] rare-earth ions in sites other than cubic are mainly responsible for the emission below RT. While the choice of L and J as good quantum numbers in systems like the one at hand is open to question, as discussed in Sec. IV D, we certainly do not rule out the possibility that some of the observed lines in both the low-temperature and high-temperature peaks are vibronic in origin.

Comparison of columns 1 and 2 in Table II shows that the spectra of the two peaks at 155 and 206°K are not identical; however, the change, i.e., the non-

appearance of the line at 5440 Å in the 206°K peak, is not sufficient to allow any firm conclusions to be drawn concerning the cause of this change.

D. Selection Rules

As mentioned in IV C, the optical emission attributed to a $^5S_2 \rightarrow {}^5I_8$ transition involves $\Delta J = \Delta L = 6$ which is strongly forbidden in the free ion. It remains forbidden even in a cubic field, since in the operator equivalent expansion for a cubic crystal field only the fourth power of the raising and lowering operators appear. However, as pointed out in the case of CaF_2: Gd^{+3},[4] the Russell-Saunders coupling scheme is used mainly for reasons of convenience and the situation is best described by a scheme intermediate between the L-S and j-j couplings. Further, recent calculations[9] have shown that the terms "cubic field" and "trigonal field" as used for rare-earth ions in CaF_2 must be viewed as a first approximation only, as it has become clear that in most cases fields of lower symmetries contribute to the total crystal field, in addition to the (large) cubic or trigonal components. Hence the application of selection rules and the choice of good quantum numbers to problems as the one at hand certainly need further study.

E. Crystal Field

It seems interesting to speculate, at this point, on the general effect of the crystal field on the energy levels of the rare-earth ion. It is known, for example,[10,11] that the ground state of the $4f^05d$ configuration of the free Ce^{+3} ion is lowered by the crystal field by about 18 000 cm^{-1}. We have indeed pointed out that crystal fields of lower symmetry have larger effect on the corresponding energy levels and accordingly the emission from ions in lower point symmetry is shifted towards lower energies (see Fig. 3 in Ref. 1). A similar effect is observed in CaF_2: Gd^{+3} (see Figs. 3 and 4 in Ref. 4); in particular, the $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transition, at tetragonal symmetry, occurs at a higher energy than the corresponding emission from ions at trigonal symmetry. In the present case of CaF_2: Ho^{+3} there seems to be a similar tendency of a total shift of the centroid of the emission towards shorter wavelengths in the 333°K emission: i.e., higher symmetry (cubic) and higher energy (shorter wavelength), in accordance with our interpretation.

V. CONCLUSION

It has been shown that in CaF_2: Ho^{+3}, as in CaF_2: Gd^{+3},[4] the thermoluminescent emission at low temperature might originate from ions in sites other than cubic. It is also most likely that the compensator may become mobile at about room temperature.

[6] W. Low and U. Ranon, in Paramagnetic Resonance, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 1, p. 167.

[7] W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) 81, 317 (1963).

[8] M. Nerenberg and M. Schlesinger, Phys. Letters 26A, 109 (1968).

[9] M. Schlesinger and M. Nerenberg, Phys. Rev. (to be published).

[10] E. Loh, Phys. Rev. 147, 332 (1966).

[11] S. Freed, Phys. Rev. 38, 2122 (1931).