The Luminescence Spectra of Triply-ionized Dysprosium and Terbium in Alkaline Earth Fluorides

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(Received May 14, 1963)

The three principal luminescence bands of the samarium(III) ion, which is embedded in alkaline earth fluorides, show, according to Tomaschek,[1] a blue shift as the matrix is changed in the sequence of calcium fluoride, strontium fluoride and barium fluoride. Here the blue shift refers to the displacement of bands towards the larger frequency side of the spectrum. Yoshimura[2] verified this regularity of the blue shift with a much greater number of bands of samarium(III) luminescence appearing in the sequence of matrices just mentioned. Furthermore, Evert[3] studied the luminescence of another rare earth ion, namely, the praseodymium(III) ion, embedded in sulfides as well as in oxides of alkaline earth elements, and put forward two suggestions, though they did not explicitly concern the luminescence in the matrices of alkaline earth fluorides. One of his suggestions was that a blue shift may also occur in the luminescence spectrum of the praseodymium(III) ion embedded in the sequence of alkaline earth fluorides with ascending lattice-constants; the other suggestion is that, with this sequence of matrices, there may be seen the "contraction of the luminescence spectrum," i. e., the decrease occurs in the frequency-intervals of the luminescence bands of the praseodymium(III) ion. This paper presents the results of investigations of the luminescence spectra of dysprosium(III) and terbium(III) ions embedded in the matrices of calcium fluoride, strontium fluoride and barium fluoride; this investigation was undertaken for the purpose of ascertaining what the effects of the crystal-field strength of these matrices on the f–f transitions of the said triply-ionized rare earths are really like.

Experimental

By means of the reactions between alkaline earth nitrates and hydrofluoric acid in aqueous solutions, precipitates of calcium fluoride, strontium fluoride and barium fluoride were prepared; they were then soaked with a nitrate solution of either dysprosium(III) or terbium(III) and calcined at about 900°C for 30 min. These rare earths were made by the Lindsay Chemical Division, the American Potash & Chemical Corporation, and were of 99.9% purity. The concentration of the rare earth ions in the matrix is always made to be about 0.1%.

The excitation to the luminescence is done in a small Urbain tube by cathode-ray bombardment at room temperature, and the luminescence thus provoked is spectrographically investigated by employing a glass-prism spectrograph of Feuss.

In the matrix-sequence of calcium fluoride, strontium fluoride and barium fluoride, the intensity of the luminescence generally decreases so markedly that, in order to make sure of a proper and detailed comparison among the luminescence spectra, the duration of the exposure to the photographic plate had to be varied, for instance,

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1) R. Tomaschek, *Z. Elektrochem.*, **36**, 737 (1930); *Physik. Z.*, **33**, 878 (1932); *Acta Phys. Polon.*, **5**, 403 (1936).

2) J. Yoshimura, *Sci. Papers, Inst. Phys. Chem. Research* (Tokyo), **23**, 224 (1933).

3) H. Evert, *Ann. Physik*, [5] **12**, 107, 137 (1932).

several minutes for the luminescence in the calcium fluoride matrix and several hours for that in the barium fluoride matrix.

Results and Discussion

Figures 1—3 are, respectively, the schematic representations of the luminescence spectra of dysprosium(III) and terbium(III) ions which are embedded in the calcium fluoride, strontium fluoride and barium fluoride matrices.

In a comparatively recent work by Chatterjee[4] on the luminescence spectra of dysprosium(III) and terbium(III) ions, calcium fluoride was selected as their matrix. From our experiments on the luminescence spectra, it is now confirmed that a fairly great number of the bands observed by him should be ascribed to the presence of praseodymium, samarium and either terbium or dysprosium as impurities in the dysprosium and terbium preparates.

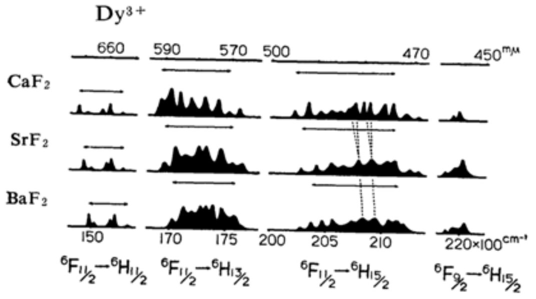

Fig. 1

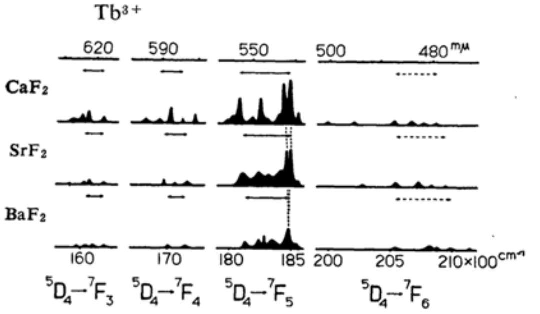

Fig. 2

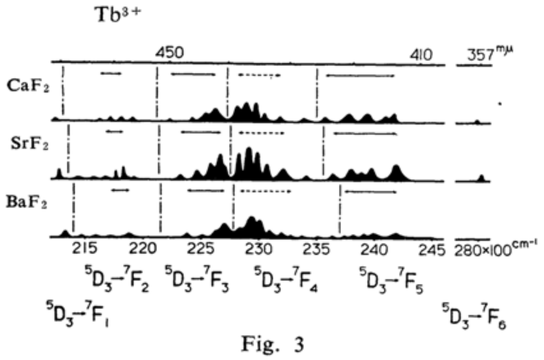

Fig. 3

Our measurements cover the frequency regions 14800～21200 cm^{-1} and 15900～26300 cm^{-1} for the luminescence of dysprosium(III) and terbium(III) ions respectively. As is shown in Table I, the total number of observed bands of the dysprosium(III) ion is 28, 26 and 27 for the luminescence found in the calcium fluoride, strontium fluoride and barium fluoride matrices respectively. Similarly, that of the terbium(III) ion is 46, 42 and 40 for the luminescence found in the calcium fluoride, strontium fluoride and barium fluoride matrices respectively.

TABLE I

	Total number of observed bands			Number of bands showing blue shift	
	CaF_2	SrF_2	BaF_2	CaF_2 →SrF_2	SrF_2 →BaF_2
Dy^{3+}	28	26	27	25	22
Tb^{3+}	46	42	40	35	33

The four systems of the bands of dysprosium(III) ions around 15100, 17300, 20800 and 22000 cm^{-1} are assigned, respectively, to the 6F11/2→6H11/2, 13/2, 15/2 and 6F9/2→6H15/2 transitions. To make these assignments of bands, the data given by Dieke and others,[5] are referred to.

Ten band-groups of the terbium(III) luminescence around 16100, 17100, 18300, 20700, 21300, 21800, 22500, 23200, 23900 and 26200 cm^{-1} are, respectively, assigned to the 5D4→7F3, 4, 5, 6 and 5D3→7F1, 2, 3, 4, 5, 6 transitions. To make these assignments of bands, the data given by Gobrecht[6] and Dieke and others[5] are taken into consideration.

The outermost electron-shell of all the triply-ionized rare earths is, as is well known, of a configuration having two 5s and six 5p electrons. Because of the shielding of this electronic structure of the closed-shell type, the f–f transitions of these ions would not be very much affected by an external force, and when these ions are embedded in various matrices, all the observed luminescence bands due to the f–f transitions are sharp and the proper correspondences between them may be ascertained comparatively easily.

When the matrix is restricted to alkaline earth fluorides with a comparatively simple structure of cubic fields (O_h^5), the lattice-constant is increased in the successive order of

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[4] N. Chatterjee, *Z. Physik*, **113**, 96 (1939).

[5] G. H. Dieke and S. Singh, *J. Opt. Soc. Am.*, **46**, 495 (1956).

[6] H. Gobrecht, *Ann. Physik*, [5] **28**, 673 (1937).

calcium fluoride, strontium fluoride and barium fluoride. Accordingly, the effects of crystal-field strength on a foreign cation embedded in the site of alkaline earth ions may be decreased in this order.

The detailed and comparative studies of the luminescence spectra of triply-ionized rare earths embedded in these alkaline earth fluorides imply the elucidation of the effects on the f—f transitions under the application of different crystal-field strengths. From the measurements described above, three items of interest may generally be settled. The first is the displacement of bands caused by changing the matrix. The second is the relative values of overall crystal-field splittings observed in the transitions with the definite total angular momentums of *J* an *J'*. The third is the determination of the splitting of certain individual bands under the influence of more intense crystal fields.

Concerning the first item, the following facts should be mentioned. If the matrix is changed in a sequence of increasing lattice-constants, namely, calcium fluoride → strontium fluoride, then 25 bands of the dysprosium(III) ion are found to follow the regularity of the blue shift as is shown in Table I. Similarly, this is the case with the 22 bands of the dysprosium(III) ion for the matrix-sequence strontium fluoride→barium fluoride. As to the luminescence of the terbium(III) ion, the blue shift is observed with 35 bands on changing the matrix calcium fluoride→strontium fluoride, and with 33 bands for the change of matrix strontium fluoride→barium fluoride.

Concerning the second item, Table II indicates that, with the decrease in the lattice-constant of the matrix in the successive order of barium fluoride, strontium fluoride and calcium fluoride, each of the overall crystal-field splittings of the 6H11/2, 13/2, and 15/2 levels of the dysprosium(III) ion is increased. Here ν and ν' are the wave number of the bands. This effect may be assumed to occur almost directly proportionately to the crystalfield strength of the matrices. In other words, if the matrices are arranged in the order of descending crystalfield strength, namely, in the sequence of calcium fluoride, strontium fluoride and barium fluoride, it can then be called a “contraction of spectrum” using Evert's term. Tables III—IV demonstrate how the relation of the socalled contraction of spectrum also holds generally for the band-systems of terbium(III) luminescence. However, there are exceptions for the two band-systems belonging to the 5D4→7F6 and 5D3→7F4 transitions, in which is seen, on the contrary, an “expansion of spectrum.”

TABLE II. MAGNITUDES OF RELATIVE CRYSTAL-FIELD SPLITTINGS $\Delta\nu$ OBSERVED IN $^6F_{11/2}\rightarrow{}^6H_{J'}$ TRANSITIONS

Dy^{3+}		CaF_2		SrF_2		BaF_2
$J'=11/2$	ν	15270 cm^{-1}		15290		15320
	ν'	14880		14930		14980
	$\Delta\nu$	390	>	360	>	340
13/2		17520		17560		17590
		16900		16940		17020
		620	≒	620	>	570
15/2		21090		21110		21150
		20210		20280		20370
		880	>	830	>	780

Finally, it is note worthy that the splitting of some individual bands under the influence of a more intense crystalfield is found in the luminescence spectra of dysprosium(III) and terbium(III) ions. The two intense bands at 20830 and 20940 cm^{-1} observed in the barium

TABLE III. MAGNITUDES OF RELATIVE CRYSTAL-FIELD SPLITTINGS $\Delta\nu$ OBSERVED IN $^5D_4\rightarrow{}^7F_{J'}$ TRANSITIONS

Tb^{3+}		CaF_2		SrF_2		BaF_2
$J'=3$	ν	16190 cm^{-1}		16190		16200
	ν'	16010		16030		16050
	$\Delta\nu$	180	>	160	>	150
4		17120		17160		17150
		16930		16980		17000
		190	>	180	>	150
5		18480		18490		18480
		18080		18100		18120
		400	>	390	>	360
6		20850		20950		21000
		20520		20540		20550
		330	<	410	<	450

TABLE IV. MAGNITUDES OF RELATIVE CRYSTAL-FIELD SPLITTINGS $\Delta\nu$ OBSERVED IN $^5D_3\rightarrow{}^7F_{J'}$ TANSITIONS

Tb^{3+}		CaF_2		SrF_2		BaF_2
$J'=2$	ν	21800 cm^{-1}		21830		21890
	ν'	21620		21660		21720
	$\Delta\nu$	180	>	170	≒	170
3		22620		22660		22700
		22230		22320		22380
		390	>	340	>	320
4		23170		23210		23280
		22810		22820		22840
		360	<	390	<	440
5		24160		24180		24190
		23560		23630		23740
		600	>	550	>	450

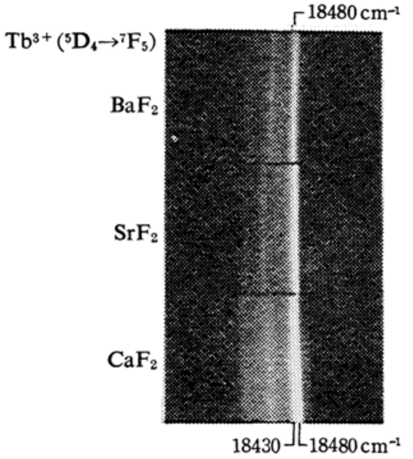

Fig. 4. Splitting of individual band in the crystalfield.

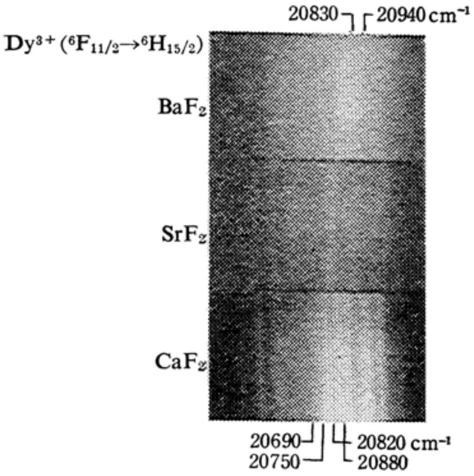

Fig. 5. Splitting of individual bands in the crystalfield.

TABLE V. SPLITTING OF INDIVIDUAL BANDS IN THE CRYSTAL FIELD

	BaF_2 cm^{-1}	SrF_2 cm^{-1}	CaF_2 cm^{-1}	$\Delta\nu$ cm^{-1}
Dy^{3+}	20830	20780	20690 20750	60
$^6F_{11/2}\rightarrow{}^6H_{15/2}$	20940	20900	20820 20880	60
Tb^{3+}	18480	18460 18490		30
$^5D_4\rightarrow{}^7F_5$			18430 18480	50

fluoride matrix are ascribed to the 6F11/2→6H15/2 transition, and these bands correspond to the two bands in the strontium fluoride matrix appearing at 20780 and 20900 cm^{-1}. On changing the matrix strontium fluoride→calcium fluoride, the band at 20780 cm^{-1} observed in strontium fluoride is found to split into two components of 20690 and 20750 cm^{-1} ($\Delta\nu=60\ cm^{-1}$) in the more intense crystalfield of calcium fluoride, while the other band of 20900 cm^{-1} in strontium fluoride similarly splits into two, of 20820 and 20880 cm^{-1} ($\Delta\nu=60\ cm^{-1}$), in calcium fluoride. It should be mentioned that the magnitude of each of these $\Delta\nu$ splittings is 60 cm^{-1}. The most intense band of terbium(III) luminescence is ascribed to a 5D4→7F5 transition and is observed at 18480 cm^{-1} in the barium fluoride matrix. In the more intense crystalfield of the strontium fluoride matrix, it splits into two components of 18460 and 18490 cm^{-1} ($\Delta\nu=30\ cm^{-1}$), while in the most intense crystalfield of the calcium fluoride matrix, it splits into components of 18430 and 18480 cm^{-1} ($\Delta\nu=50\ cm^1$). It should be emphasized that the magnitude of these splittings, namely 30 and 50 cm^{-1}, may be taken as the approximate measure of the relative strength of the crystalfield for the matrices of barium fluoride, strontium fluoride and calcium fluoride.

Summary

(i) The luminescence spectra of dysprosium(III) and terbium(III) ions have been measured in the cubic field (O_h^5) of calcium fluoride, strontium fluoride and barium fluoride under excitation by cathode-ray-bombardment.

(ii) The displacement of the luminescence bands of dysprosium(III) ion has been studied with relation to the matrices mentioned above, a blue shift being observed, with 25 and 22 bands as the matrix was changed in successive sequences of calcium fluoride to strontium fluoride and strontium fluoride to barium fluoride respectively. Similarly, this was the case with 35 bands of the terbium(III) luminescence when, the matrix was changed from calcium fluoride to strontium fluoride, and with 33 bands for that from strontium fluoride to barium fluoride.

(iii) The magnitude of the relative crystalfield splittings $\Delta\nu$ of the luminescence bands of dysprosium(III) and terbium(III) ions was reported in relation to the increasing strength of the crystal field, i. e., in the sequence of matrices barium fluoride, strontium fluoride and calcium fluoride. For the dysprosium(III) luminescence, the crystalfield splittings observed in the 6F11/2→6H11/2, 6F11/2→6H13/2 and 6F11/2→6H15/2 transitions had a tendency to increase in the matrix-sequence barium fluoride, strontium fluoride and calcium fluoride. In the case of the terbium(III) luminescence, variations similar to that found in the dysprosium(III) luminescence took place in the crystalfield splittings of the 5D4→7F3, 5D4→7F4,

5D4→7F5, 5D3→7F2, 5D3→7F3 and 5D3→7F5, transitions, while the reverse was the case with the 5D4→7F6 and 5D3→7F4 transitions.

(iv) It was found that the band appearing at 18480 cm^{-1} in the luminescence spectrum of the terbium(III) ion embedded in barium fluoride splits into its respective two components when the terbium ion was embedded in matrices of strontium fluoride and calcium fluoride with a more intense crystalfield strength. The magnitudes of these splittings, 30 and 50 cm^{-1} as observed in strontium fluoride and calcium fluoride respectively, are presumably proportional to the differences between the crystalfield strength for barium fluoride, strontium fluoride and calcium fluoride.

The authors wish to thank Professor S. Nagakura, Professor S. Sugano and Professor S. Shionoya of the Institute for Solid State Physics, the University of Tokyo, for their interest and helpful discussions.

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