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Optical Studies of Dy^{+3} - Doped Calcium Fluoride[†]

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High-resolution thermoluminescence spectra for individual glow peaks, luminescence, and luminescence excitation spectra at liquid-nitrogen temperature are presented for the CaF_2 : Dy^{+3} system. A qualitative interpretation of the results is offered and discussed.

I. INTRODUCTION

In a previous paper[1] from our research group pertaining to CaF_2: Gd^{+3}, the thermoluminescence emission was investigated. It was shown that, depending on the crystal-growth conditions and thermal history, rare-earth ions in sites of different symmetries may be responsible for the emission even at low (77 °K) temperatures. In a subsequent publication,[2] theoretical results were presented. supporting the interpretation given in the first paper.

In the present work we investigated the CaF_2: Dy^{+3} system by means of thermoluminescence techniques coupled with measurements of luminescence and luminescence excitation spectra.

It will be evident that here too, as in the case of the CaF_2: Gd^{+3} system, the thermoluminescence probably originates from Dy^{+3} ions situated in sites of different symmetry.

II. EXPERIMENTAL

Crystals used in the present work were obtained from the Harshaw Chemical Co. (with Dy^{+3} concentration of about 0.1%). The concentration of other impurities in these crystals was less than 10 ppm.[3] The experimental procedure for obtaining the general glow curve and its spectral distribution were as described elsewhere[1] except for the dispersing instrument which was a grating spectrograph[4] with a low *f* number (about 2.5) and a medium-high resolution (better than 0.5 Å in first order). The x-ray source was a copper-target x-ray tube operated at 50-kV peak and 14 mA.

Luminescence spectra were taken from non-x-irradiated crystals in the following way. The exciting light source was a 1000-W xenon lamp. The light from the lamp was passed through a "Leiss" double monochromator. The double monochromator was used to minimize the amount of stray light. The entrance slit of the double monochromator was typically set at 0.3 mm, the middle slit at 0.35 mm, and the exit slit at 0.4 mm. The spectral width of the emerging light illuminating the crystal was about 40 cm^{-1} in the spectral region of the experiments. The emitted luminescence was detected by either a photographic plate or an EMI-type 6256B photomultiplier through the grating spectrograph set at the proper wavelength region.

In the luminescence-excitation-spectrum measurements, a similar procedure was followed except that the wavelength of the exciting light was changed by mechanically driving the prism tables in the double monochromator.

III. RESULTS

Figure 1 is the glow curve of CaF_2: Dy^{+3} single crystals between 77 and 300 °K. Essentially three main glow peaks appear in the glow curve at 110, 149, and 180 °K.

The glow curve in Fig. 1 was obtained from a crystal that was x irradiated for 90 min at liquid-nitrogen temperature. The heating rate was 11 °K/min.

Figure 2(a) is the microdensitometer trace of the thermoluminescence emission spectrum in the "blue-green" region. Identical results in this part of the spectrum were obtained separately for each of the three main glow peaks (see Fig. 1). In Fig. 2(b) we present the microdensitometer trace of the

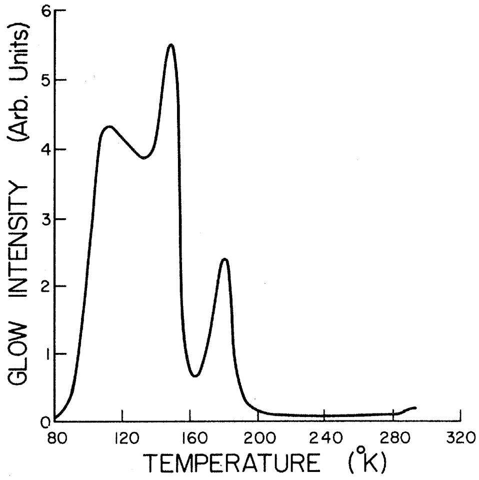

FIG. 1. Thermoluminescence glow curve of CaF_2 : Dy^{+3} crystal x irradiated for 90 min at liquid-nitrogen temperature.

"yellow" portion of the thermoluminescence emission. Here again essentially identical results were obtained separately for all glow peaks between 77 and 300 °K.

In Figs. 3(a) and 3(b) we present the microdensitometer traces of the spectral distribution of the luminescence in the blue-green and yellow portions of the spectrum, respectively. These were obtained by illuminating the non-x-irradiated crystal with light of wavelength in the 3515-Å region and at liquid-nitrogen temperature.

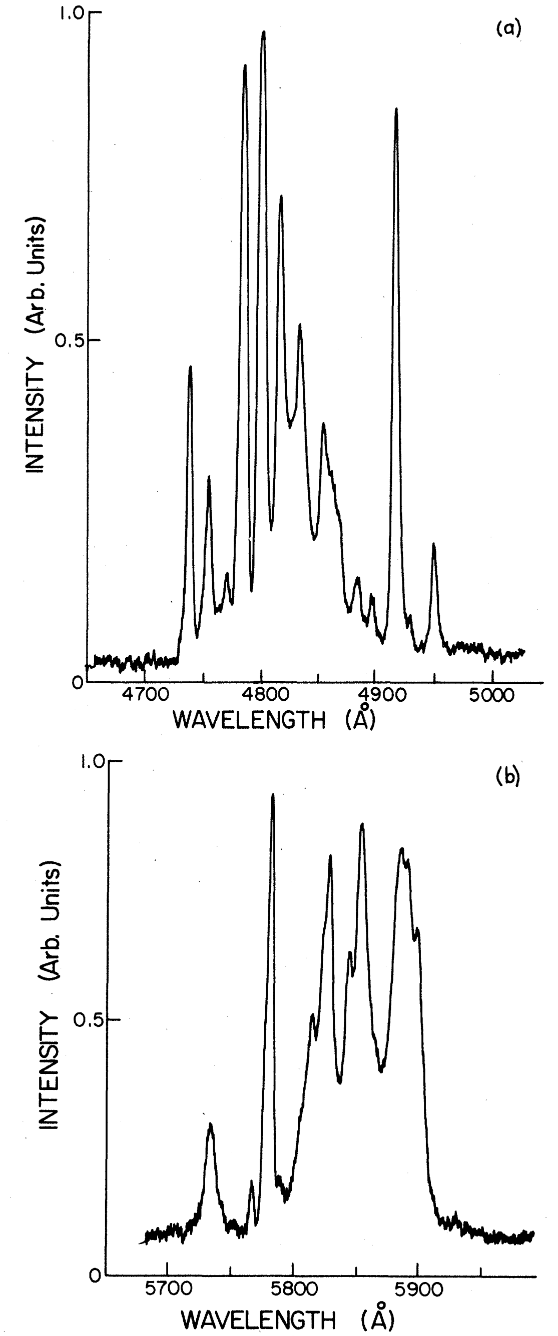

FIG. 2. (a) The microdensitometer trace of the spectral composition of the thermoluminescence in the "blue-green" spectral region. An identical spectrum was found for all the glow peaks (see Fig. 1). (b) The same as (a) except in the "yellow" region of the spectrum.

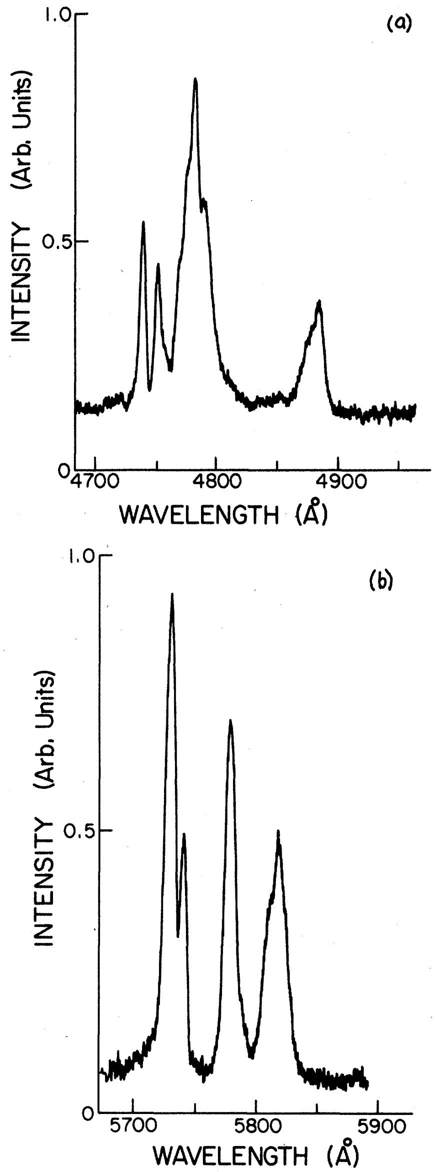

FIG. 3. (a) The microdensitometer trace of the spectral composition of the "blue-green" luminescence (excited with light of $\lambda = 3515$ Å) at liquid-nitrogen temperature. (b) The same as (a) except in the "yellow" spectral region.

Figure 4 is a direct recorder tracing of the yellow luminescence excitation spectrum. An identical spectrum was obtained for the excitation of the blue-green emission, except for the group of peaks at 4700 Å which naturally appear in the yellow excitation spectrum only. (This band is due to yellow luminescence obtained by illuminating with wave-

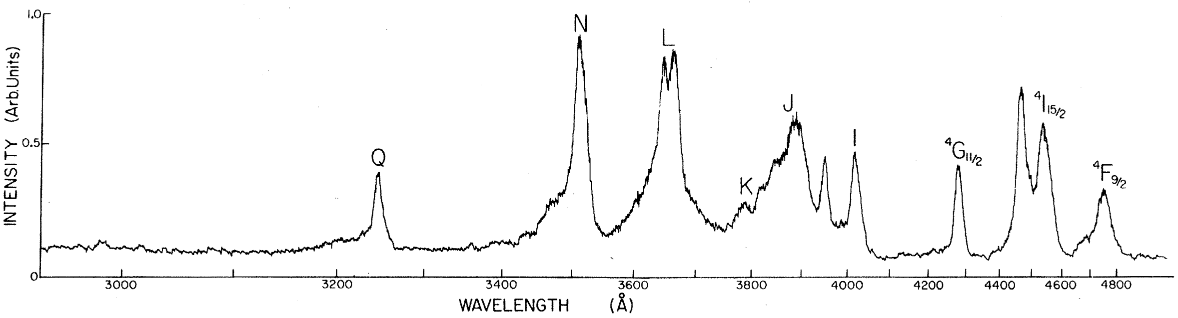

FIG. 4. The excitation spectrum of the "yellow" luminescence obtained at liquid-nitrogen temperature. Labeling of peaks after Ref. 5.

length corresponding to the blue-green emission.) Labeling of peaks is after Dieke.[5]

IV. ANALYSIS OF RESULTS AND DISCUSSION

The electron configuration of Dy^{+3} is $4f^9$ with a ground state ${}^6H_{15/2}$. An excited state ${}^4F_{9/2}$ exists[6] at about 21 000 cm^{-1}. The observed blue-green emission, both in thermoluminescence and luminescence, corresponds to the ${}^4F_{9/2}$-${}^6H_{15/2}$ transition. Still another excited state ${}^6H_{13/2}$ exists at about 3500 cm^{-1}. As we shall elaborate below, we attribute the yellow emission to the ${}^4F_{9/2}$-${}^6H_{13/2}$ transition. Both spectra are, of course, Stark split in the CaF_2 matrix. As suggested earlier,[1,7,8] the thermoluminescence in the CaF_2: Dy^{+3} crystal takes place in the following way. X rays reduce the Dy^{+3} ion to the Dy^{+2} state. The resulting hole is trapped in a nearby site (trap). Different kinds of such traps can exist in the crystal with varying activation energies corresponding to the different glow peaks. Upon heating the crystal, the hole is released and it recombines with the Dy^{+2} ion to give rise to Dy^{+3} ion in an excited state. Subsequently the ion relaxes to its ground state emitting characteristic radiation. Hence, one expects the thermoluminescence emission to be characteristic of the triply ionized rare-earth (RE^{+3}) ion.

The thermoluminescence in CaF_2: Dy^{+3} was studied by Kiss and Staebler[7] and later by Merz and Pershan.[8] Yellow emission in the thermoluminescence was not reported by Kiss and Staebler. Neither was it mentioned in the work of Merz and Pershan. As mentioned above, we tentatively attribute it to the ${}^4F_{9/2}$-${}^6H_{13/2}$ transition. This is supported by our findings that the luminescence excitation spectra for both blue-green and yellow emissions are identical in every detail which, we feel, offers convincing proof that they both originate at the same excited-state level, viz., ${}^4F_{9/2}$. Further, the fact that illuminating with light corresponding to the blue-green emission was enough to yield the yellow luminescence eliminates the possibility for the yellow emission to originate at any level higher than the ${}^4F_{9/2}$, which leaves the only possibility for it to be the ${}^4F_{9/2}$-${}^6H_{13/2}$ transition.

It should be pointed out that there are very many levels of Dy^{+3} above 21 000 cm^{-1} but their density and complexity is so high (see Fig. 4; see also Ref. 6) that a satisfactory interpretation without a great deal of additional theoretical and experimental work seems at present virtually impossible. The interpretation of levels below 15 000 cm^{-1} seems now fairly established, however. There was in the past some confusion because of the near coincidence of the ${}^6F_{9/2}$ with the ${}^6H_{7/2}$ level, and the ${}^6F_{11/2}$ with the ${}^6H_{9/2}$ level.

The crystal field splittings are considerably influenced by J mixing, and one must take that into account before any reasonable agreement between calculated and observed levels can be arrived at.

In view of all these we shall attempt, at present, to offer only a qualitative interpretation for our results.

A comparison between Fig. 2(a) in the present work and Fig. 6(a) in Ref. 8 shows that essentially all the lines observed by Merz and Pershan[8] appear in our spectrum as well with the exception that their line at 4786 Å is composed of two components. In addition our spectrum includes many more lines not observed by either Merz and Pershan[8] or Kiss and Staebler.[7] Accordingly we suggest that the thermoluminescence spectrum exhibited by our crystals represents a mixture of both cubic and possibly sites of lower symmetries.

Careful comparison between Fig. 3(a) in our work with Fig. 6(b) of Ref. 8 [or Fig. 1(b) in Ref. 7] reveals an almost identical profile with the difference that our spectrum has perhaps a somewhat poorer resolution but a considerably better intensity.

Our interpretation here is that since excitation (see above) took place in a very narrow spectral range, one can expect that Dy^{+3} ions only in sites of one kind of symmetry (the one that happens to absorb in that wavelength) would be excited. Accordingly the lines observed in Fig. 3(a) constitute a "true" subset of those in Fig. 2(a).

In addition, the lines in Fig. 3(b) are observed to be a true subset of the ones in Fig. 2(b). In other words we suggest that our luminescence spectrum is due to the emission of Dy^{+3} ions in sites of one- (lower than cubic) point symmetry. This means that in accordance with our previous[2] suggestions, sites of different symmetries can be responsible for thermoluminescence emission even at temperatures close to that of liquid nitrogen. Attempts to excite luminescence of Dy^{+3} in sites of cubic symmetry only were not conclusive due to the very low intensity of the emission involved.

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[*] Holder of a Province of Ontario Graduate Fellowship.

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

[2] M. Schlesinger and M. Nerenberg, Phys. Rev. 178, 568 (1969).

[3] Crystals from a different source (Optovac) were used also. Essentially identical results to those from the Harshaw samples were obtained from these crystals.

[4] A detailed description of the spectrograph which was constructed in our laboratory can be secured by writing to one of us (M. S.).

[5] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience, New York, 1968), pp. 268–279.

[6] Reference 5, p. 142.

[7] Z. Kiss and D. L. Staebler, Phys. Rev. Letters 14, 691 (1965).

[8] J. L. Merz and P. S. Pershan, Phys. Rev. 162, 217 (1967).

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Electron Paramagnetic Resonance of Several Rare-Earth Impurities in the Cubic Perovskite KMgF$_3$[†]

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The electron paramagnetic resonance spectra of doped KMgF$_3$ single crystals containing Yb^{3+}, Tm^{2+}, Er^{3+}, Dy^{3+}, and Gd^{3+} have been observed at 9 GHz. Cubic symmetry sites have been identified for these ions and the data indicate that the Yb^{3+}, Tm^{2+}, Er^{3+}, and Dy^{3+} substitute for the sixfold-coordinated Mg^{2+} ion, but that the gadolinium probably substitutes for a twelvefold-coordinated K^{1+} ion. Noncubic symmetry sites were also observed for Yb^{3+}, Er^{3+}, and Gd^{3+}. Hyperfine structure for the isotopes ^{171}Yb, ^{173}Yb, ^{169}Tm, ^{167}Er, ^{161}Dy, and ^{163}Dy was identified, and in some cases superhyperfine interactions with the fluorine ligand ions were observed with good resolution.

INTRODUCTION

It is well known that the fourth-order term in the expansion of the crystal-field potential has a different sign for sixfold cubic coordination as opposed to fourfold, eightfold, or twelvefold cubic coordinations.[1] For twelvefold coordinations, the sixth-order term has a different sign than for the other three types of coordination. These sign reversals lead to a different ground state for a substitutional paramagnetic impurity in sixfold coordinations than for the same ion in the other coordinations. An electron paramagnetic resonance (EPR) study of a particular rare-earth impurity ion in cubic crystalline environments with different coordinations would therefore enable different ground-state resonances to be observed for this ion. The cubic perovskite structure of KMgF$_3$ ($a_0 = 3.973$ Å) is ideal for a study of this nature.[2] The structure may be visualized as K^{1+} ions at the corners of a cube with a Mg^{2+} ion at the body center and F$^-$ ions at the face-center positions. The Mg^{2+} ion has six F$^-$ nearest neighbors along $\langle 100 \rangle$ directions, while the K^{1+} ion has twelve F$^-$ nearest neighbors along $\langle 110 \rangle$ directions. Assuming that the necessary charge compensation does not occur nearby, a rare-earth ion residing in a magnesium site would experience a sixfold-coordinated cubic crystal field; if the potassium site were occupied, the cubic field would be twelvefold coordinated. The EPR spectrum obtained for the rare-earth impurity should clearly distinguish between these two types of cubic coordination. Further, any observed superhyperfine interactions with the fluorine ligand ions would be an additional aid in determining the impurity site location. Although the $4f$ electronic wave functions are fairly well localized, superhyperfine structure has been observed in the eightfold-coordinated fluorite structure of CaF$_2$ for Ce^{3+}($4f^1$),[3] Tb^{3+}($4f^8$),[4] Tm^{2+}($4f^{13}$),[5] and Yb^{3+}($4f^{13}$).[6] Superhyperfine structure has also been seen for Gd^{3+} in CaF$_2$ crystals that have been subjected to strains.[7] Accordingly, we have doped KMgF$_3$ single crystals with Yb^{3+}, Tm^{2+}, Er^{3+}, Dy^{3+}, and Gd^{3+} and observed the