Photoionization and trapping of electrons in the system BaF$_2$:Eu:Sm

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The mechanism of electron transfer in the doubly doped BaF$_2$:Eu:Sm sample is investigated. The electrons are ionized at 77 K from divalent Eu^{2+} by photons with appropriate energy, then trapped by some trivalent Sm^{3+}:F$^-$ centers to form unstable Sm^{2+}:F$^-$ complexes. Some less-quantitative observations showed that some uncompensated Sm^{3+} was present and was a much better trap than the compensated Sm^{3+}. An accidental impurity of Ce^{3+} with the same type of charge compensator as Sm^{3+} proved to be a very poor trap compared to compensated Sm^{3+}. The observed absorption and emission spectra of the Sm^{2+}:F$^-$ unambiguously show that the fluoride compensator is in the next-nearest-neighbor position, namely, the C_{3v} site. The fluoride compensator decreases the photoionization threshold of Sm^{2+} by at least a quarter of an eV and quenches the fluorescence at much lower temperature. Upon warming the sample to room temperature the compensator diffuses away. The absolute photoionization efficiency of divalent Eu in BaF$_2$:Eu:Sm crystal has been measured to be 9.7% at 298 K and 6.0% at 77 K temperatures.
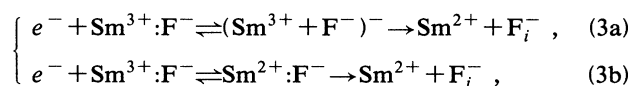
I. INTRODUCTION

It is well known that europium and samarium have stable oxidation states of 2 and 3, respectively, in crystals. Divalent Eu is more stable than divalent Sm due to its half-filled ($4f^7$) valence shell. When Eu and Sm are doped together into fluorite crystals (e.g., in BaF$_2$) most of the Eu is divalent while most of the Sm is trivalent. For the trivalent Sm or Eu a charge compensator is required in order to maintain a neutral system. If the crystals are grown in an oxygen-free atmosphere, the compensators are interstitial fluorides which tend to stay close to trivalent ions because of the attractive Coulomb forces. However, we can always find some uncompensated trivalent sites (or remotely compensated sites).

In the system described above the following photoreaction was reported by Feofilov,[1] and later Welber[2] in a CaF$_2$ host:

$$\text{Eu}^{2+} + \text{Sm}^{3+} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} \text{Eu}^{3+} + \text{Sm}^{2+} . \tag{1}$$
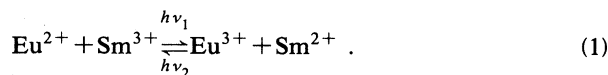
By irradiating with either 4.9 eV (254 nm) light or 3.9 eV (313 nm) light, the forward reaction or the backward reaction was observed, respectively. Photoconductivity and quantum-yield measurements showed that a divalent impurity absorbs the appropriate photon (either 4.9 eV light for Eu^{2+} or 3.9 eV light for Sm^{2+}), and photoionizes and ejects an electron into the conduction band. Subsequently, a trivalent impurity, either Eu^{3+} or Sm^{3+}, will act as a trap and capture the free conduction-band electron, thus forming the corresponding divalent impurity. Since the majority of trivalent impurities are originally compensated by the fluoride ions, the electron trapping process will certainly involve the movement of this compensator. We use the following equations to elucidate the whole process of the forward photoreaction in Eq. (1):

$$\text{Eu}^{2+} \overset{h\nu}{\rightleftharpoons} \text{Eu}^{3+} + e^- , \tag{2}$$

$$\begin{cases} e^- + \text{Sm}^{3+}\text{:F}^- \rightleftharpoons (\text{Sm}^{3+} + \text{F}^-)^- \rightarrow \text{Sm}^{2+} + \text{F}_i^- , & (3a) \\ e^- + \text{Sm}^{3+}\text{:F}^- \rightleftharpoons \text{Sm}^{2+}\text{:F}^- \rightarrow \text{Sm}^{2+} + \text{F}_i^- , & (3b) \end{cases}$$

$$\text{Eu}^{3+} + \text{F}_i^- \rightarrow \text{Eu}^{3+}\text{:F}^- . \tag{4}$$

Equations (3a) and (3b) represent two possible reaction paths, where F$_i^-$ stands for a free interstitial ion. In Eq. (3a), the Sm^{3+}:F$^-$ pair dissociate first in the presence of the electron being trapped, followed by the capture of the electron by Sm^{3+}. In Eq. (3b), an intermediate product, Sm^{2+}:F$^-$, is formed. It then breaks up with the diffusion of the fluoride compensator.

In the SrF$_2$:Eu:Sm system Fuller and McClure[3] recently found that this photoreaction process has an activation barrier of about 0.34 eV. This activation energy was attributed to the trapping process as expressed in Eq. (3a). The dissociation energy of the Sm^{3+}:F$^-$ complex itself was reported as $E_d = 0.57$ eV in SrF$_2$.[4] It indicates that the presence of the electron facilitates the breakup of the complex. But it is still possible for reaction (3b) to happen with this activation energy.

In the present studies on BaF$_2$:Eu:Sm we have verified that Eq. (3b) is the real reaction path. The absorption (Sec. III A) and emission (Sec. III B) spectra as well as photoionization characteristics (Sec. III C) clearly demonstrate the formation of the unstable Sm^{2+}:F$^-$ complex after ionizing Eu^{2+} ions at 77 K. The disappearance of the above observed features after warming the ionized crystal from 77 K to room temperature indicates that the fluoride compensators diffuse away from Sm^{2+} ions which actually do not need to be compensated. The diffusing F$^-$ ions will finally be trapped by cubic Eu^{3+} ions (Sec. III D).

In addition, the absolute photoionization efficiency of Eu^{2+} in a BaF$_2$:Eu:Sm sample has been measured at both 298 and 77 K (Sec. III E). Compared with the

SrF$_2$:Eu:Sm sample in which ionization efficiency at 298 K is more than 1000 times larger than that at 77 K, in a BaF$_2$ host the efficiencies at both temperatures differ only by a factor of 1.6.

II. EXPERIMENTAL DETAIL

All the samples were purchased from Optovac. The BaF$_2$ crystal doped with nominal concentrations of 0.01 mol % Eu and 0.01 mol % Sm (or 0.02 mol % Sm in the other one) was found to contain cerium impurity. The absorption spectra were obtained on a Cary model 14 double-beam spectrophotometer and a Hewlett-Packard 8450A (HP) diode array spectrophotometer.

For the fluorescence studies, the second harmonic of Nd:YAG laser beam of 10 Hz was focused into a hydrogen Raman cell to generate the first anti-Stokes shift at 22 952 cm^{-1}. This frequency was then further doubled with a β-barium borate (BBO) crystal to 45 904 cm^{-1}. The final pulse had an energy of about 0.1 mJ. Making use of this radiation, a fresh BaF$_2$:Eu:Sm sample was irradiated from one side by using this radiation to form Sm^{2+}:F$^-$ complexes. Subsequently it was excited in its first absorption band with a 150-W xenon lamp filtered with a couple of bandpass filters. The fluorescence was focused onto the slit of a 2-m McPherson spectrometer equipped with an R928 red-sensitive photomultiplier. The wavelength scan and photomultiplier tube (PMT) signal collection were controlled by a HP microcomputer.

A 2000-W xenon lamp was used to photoionize divalent europium ions in some experiments. An H-10 uv single monochromator was used for selecting uv light near the absorption maximum of the Eu^{2+} ion (at 233 nm with a bandwidth of 8 nm).

The excitation spectra of trivalent europium were obtained using a nitrogen laser-pumped dye laser controlled by the HP microcomputer in the 520–530 nm region which covers the $^7F_0$–$^5D_1$ transitions of Eu^{3+}. The fluorescence was monitored by a photomultiplier fixed behind a double monochromator at 562 nm corresponding to $^5D_0$–$^7F_1$ emission. Wavelength calibrations were performed using several neon optogalvanic transition lines as absolute standard and a 1-cm^{-1} free spectral range étalon as relative calibration.

III. RESULTS AND DISCUSSION

A. Absorption spectra

The spectroscopic characteristics of Sm and Eu are well known.[5] Figures 1(a) and 1(b) are the absorption spectra of divalent Sm^{2+} and Eu^{2+} in BaF$_2$, respectively. Since the Eu^{2+} and Sm^{2+} ions experience an eightfold-coordinated cubic environment, the $5d$ orbital is split into lower E_g and upper T_{2g} components. The ground state ^8S of Eu^{2+} arises from the $4f^7$ configuration. The two broad bands arise from the $4f^7$–$4f^6 5d$ transition. The two excited states $|^7F_J, E_g\rangle$ and $|^7F_J, T_{2g}\rangle$ are formed as the result of the coupling of the $4f^6$ core with a $5d$ electron. The bands at 586 and 400 nm of the Sm^{2+} ion involve transitions from $4f^6$ ($^7F_0$) ground state to the

$|E_g, 4f^5(6H)\rangle$ and $|E_g, 4f^5(6F)\rangle$ excited states, respectively, while the 300-nm band is a transition to the $|T_{2g}, 4f^5(6H)\rangle$ excited state.

Figure 1(c) shows the spectrum of an unirradiated BaF$_2$:Eu:Sm sample containing 0.01 mol % each of Eu and Sm nominally. It indicates that a large amount of Eu is in divalent form and none of the Sm exists in divalent form. The peak at 290 nm was identified to be the $4f$–$5d$ (E_g state) absorption peak of trivalent cerium which appeared as an impurity in the crystal. The crystal was irradiated using 233-nm light from a 2000-W xenon lamp through a single monochromator at room temperature for 140 min. The beam intensity is 12.5 mW/mm^2. The appearance of Sm^{2+} absorption bands at 568 and 400 nm and the decrease in absorption peak of Eu^{2+} are shown in Fig. 1(d). It is very clear that the absorbance of Ce^{3+} ions does not show any change in this spectrum. This means that Sm^{3+} ions serve as much more efficient traps than Ce^{3+} ions do for free electrons during this photore-
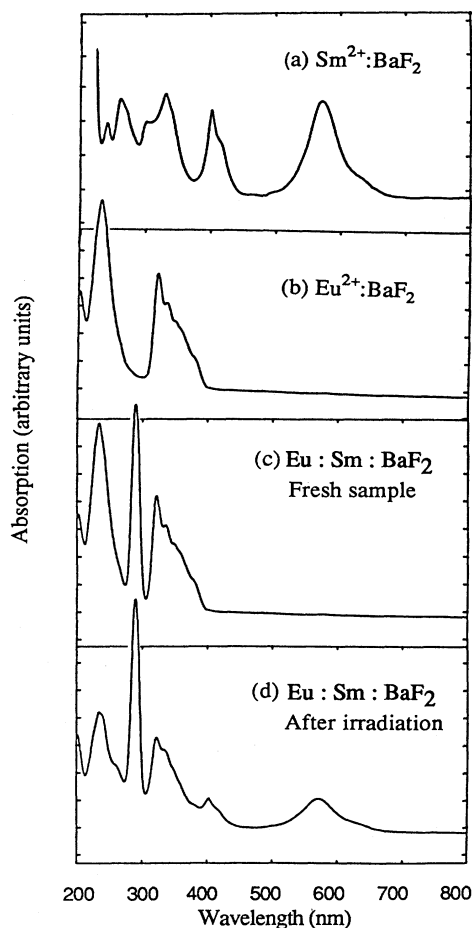

FIG. 1. Absorption spectra at room temperature: (a) BaF$_2$:Sm^{2+}, (b) BaF$_2$:Eu^{2+} sample, (c) BaF$_2$:Sm:Eu sample before irradiation. The spectrum is similar to (b) with the exception of a peak at 290 nm due to Ce^{3+} impurity. (d) Sample in (c), after irradiation at 233 nm, the Sm^{2+} absorption features appear while Eu^{2+} absorption peaks decrease. Ce^{3+} absorption remains unaltered.

action, although the divalent cerium ions were found quite stable in CaF_2 at room temperature.[6]

A fresh sample was mounted on the cold finger of a Dewar and kept at a temperature of 77 K while the sample was irradiated with 233-nm uv light. After irradiation an absorption spectrum in the region of 520 to 640 nm was taken, as curve (a) in Fig. 2 with the maximum at 583.4 nm. The sample was annealed at room temperature overnight and cooled to 77 K. The whole absorption band shifted to the blue and the peak maximum changed to 576.1 nm, as can be seen in Fig. 2 curve (b), which is in fact identical to the spectrum of a singly doped Sm^{2+}:BaF_2 crystal. We have also looked at the 400-nm absorption peak. It shifted in the same direction as the 580-nm peak. This agrees with the assignment that both peaks belong to the same $5d$ (E_g) state. We were not able to see how the $5d$ (T_{2g}) state shifts or splits in the experiment because it overlaps with strong absorption peaks of Eu^{2+} and Ce^{3+} ions.

The change of the divalent Sm^{2+} absorption peak is obvious evidence that the divalent Sm is compensated by its original interstitial fluoride compensator after irradiation at 77 K. The value of 10 Dq of Sm^{2+} $5d$ electron is about 15 000 cm^{-1}. The redshift of 220 cm^{-1} means that Dq increased and that the compensator could be in the C_{3v} position rather than the C_{4v} because the C_{4v} compensator would decrease the 10 Dq value and cause splitting of the E_g state. Taking an R^{-5} dependence of 10 Dq and considering one out of eight positions on the cube, we estimated a shift of 100 cm^{-1}, which agrees with our observation in order of magnitude.

If the sample is warmed to room temperature this compensator diffuses away because of the extra negative charge in this center. The diffusing fluoride will be finally trapped by trivalent Eu^{3+} which is still at a cubic site since an electron was ionized (see Sec. III D).
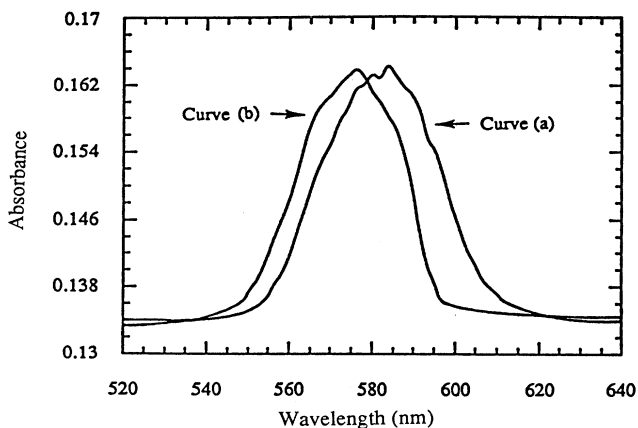
B. The emission spectra of the Sm^{2+} ion

From the absorption spectrum we have tentatively assigned the symmetry of the compensated Sm^{2+} complex to be C_{3v}. But the assignment is not very certain because the strong f-d interconfiguration transition band is too broad. Fortunately the emission spectrum of Sm^{2+} in BaF_2 consists of several discrete lines. The lowest excited state of Sm^{2+} is a $^5D_0$ state of the $4f^6$ valence electron configuration. The fluorescence starting from this state to the ^7F_J ground-state multiplet components gives rise to some sharp emission lines. The most intense one involves the $^5D_0$-$^7F_1$ transition. The energy-level diagram of a $4f^6$ free ion and in various crystal fields is shown in Fig. 3. If Sm^{2+} is compensated locally by interstitial fluoride, we would expect to see some emission lines split due to the lowering of symmetry caused by the presence of the F^- compensator.

The emission spectrum was recorded at 77 K as in Fig. 4(a) after irradiating the BaF_2:Eu:Sm sample for 1 h with 218-nm light as described in the experimental section. To our surprise the spectrum is very similar to that reported by Wood and Kaiser[7] for their Sm^{2+}:BaF_2 in which Sm^{2+} should not be compensated. The only difference is that the $^5D_0$-$^7F_0$ line is absent in our spectrum. The two sharp lines are attributed to the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_3$ transitions, respectively. The three sets of broad double peaks were assigned to vibronic sidebands due to transverse-optical phonon modes of the BaF_2 host. The first set is associated with the $^5D_0$-$^7F_1$ electronic transition. The last two sets are apparently related to the E_g
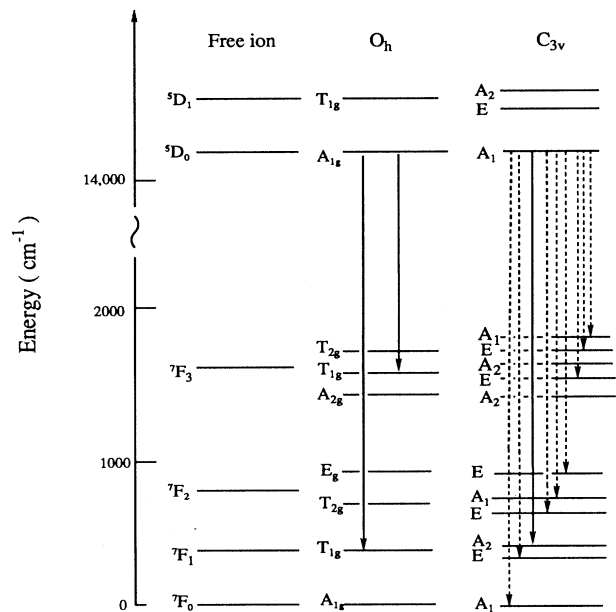

FIG. 2. One of the absorption peaks of Sm^{2+} at 77 K in the BaF_2:Sm:Eu sample: Curve (a): after the sample was irradiated at 77 K with 233 nm light. Curve (b): the sample was then annealed to room temperature, and cooled to 77 K again. It becomes the normal Sm^{2+} absorption peak.

FIG. 3. Schematic energy-level diagram of $4f^6$ electronic configuration of the Sm^{2+} ion. The free ion ^7F_J manifolds are split in both the O_h and C_{3v} crystal fields. The observed emissions are drawn with dotted arrow lines which indicate electric dipole transitions. The solid arrow lines shows the magnetic dipole transitions.

and T_{2g} states of the $^7F_2$ level. However, the direct transitions to these two states are strictly forbidden.

The sample was further cooled to 20 K. The fluorescence spectrum is shown in Fig. 4(b). The expected emission spectrum of compensated Sm^{2+} ions appears along with that of uncompensated Sm^{2+} ions. The $^5D_0-^7F_0$ transition appears intensely at 14 630 cm^{-1}, in exactly the same position as in Wood and Kaiser's paper. The $^5D_0-^7F_1$ line splits into two lines. The $^5D_0-^7F_2$ transitions appear at 13 954, 13 921, and 13 621 cm^{-1}. Near the $^5D_1-^7F_3$ line of uncompensated Sm^{2+}, we found three other sharp transitions. There are quite a few new vibronic broadbands coming with the uncompensated Sm^{2+} ion emission spectrum. Table I lists the frequencies of all observed electronic zero-phonon lines and peaks of the broad vibronic transitions.

All these splittings clearly reveal the symmetry of $Sm^{2+}:F^-$ center and the nature of its electronic transitions. There are two well-known compensating positions for interstitial fluoride in fluorite-structure crystals doped with trivalent rare-earth ions. One is along the $\langle 001 \rangle$ axis and the other along the $\langle 111 \rangle$ axis. They form centers having C_{4v} and C_{3v} symmetries, respectively, as shown in Fig. 5. It is difficult to derive structure information from the splitting of $^7F_1$ state since either C_{3v} or C_{4v} crystal field splits $^7F_1$ into two levels which were observed in the emission spectrum.

Now looking at the $^5D_0-^7F_2$ transitions, we see three lines which match the splitting pattern of C_{3v} symmetry [see Figs. 3 and 4(b)]. A pair of peaks at 13 954 and 13 921 cm^{-1} result from the splitting of the T_{2g} triplet
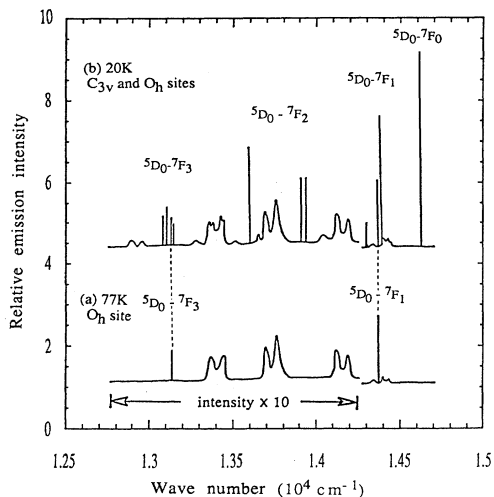
state of O_h into A_1 and E of C_{3v}. The single peak at 13 621 cm^{-1} on the lower-energy side arises from the nonsplit E_g doublet state. This also manifests that the $T_{2g}(^7F_2)$ state lies lower than $E_g(^7F_2)$ state in the eightfold cubic field. All of the three transitions are electric dipole allowed according to the selection rules. If the Sm^{+2} ion were in a site of C_{4v} symmetry, the $^7F_2$ manifold would split into four levels, A_1, B_1, B_2, and E. But the transitions from $A_1(^5D_0)$ to both B_1 and B_2 are forbidden for either electric or magnetic dipole transitions. Thus we would have seen only two $^5D_0-^7F_2$ emission lines instead of the observed three lines. Thus it is concluded that the $Sm^{2+}:F^-$ complex forms a site of C_{3v} symmetry. In other words, the Sm^{3+} ion is trigonally compensated originally by an interstitial fluoride if there is no symmetry change during the electron-trapping process. Dorenbos et al.[4] have concluded from using ionic thermocurrent measurements that in BaF_2 crystal the compensation of trivalent rare-earth ion is trigonal in nature. Their experiments included La, Eu, Gd, and Yb ions. Since Sm is located between La and Eu in the

TABLE I. The frequencies of fluorescence of the Sm^{2+} ion in both O_h and C_{3v} sites. The J values in the first column designate the $^5D_0-^7F_J$ zero-phonon transitions. The rest are the peak frequencies of vibronic broad bands.

J values of ground states	Emission frequency (cm^{-1})		Energy levels (cm^{-1})
	O_h site	C_{3v} site	
0		14630	0
		14459	
		14446	
	14465		
	14432		
	14395		
1		14389	241
1	14374		256
	14331		
1		14303	327
	14211		
	14126		
		14056	
2		13954	676
2		13921	709
		13879	
	13771		
	13708		
		13673	
2		13621	1009
		13534	
	13461		
		13437	
		13412	
	13392		
3		13180	1450
3	13164		1466
3		13131	1499
3		13103	1527
		12983	
		12924	

FIG. 4. The emission spectra of the Sm^{2+} ion in BaF$_2$:Sm:Eu sample after irradiation with a 218-nm beam. Uncorrected for the response of the detector and spectrometer. (a) The spectrum at 77 K. It is the same as the spectrum of our singly doped Sm^{2+}:BaF$_2$ sample. This means that the crystal contains some uncompensated Sm^{3+} ions originally which are of O_h symmetry. (b) The spectrum at 20 K. The new emission features come from the charge compensated Sm^{2+} ion with C_{3v} symmetry. Some sharp zero-phonon lines become allowed and some are split at lower symmetry.

(a) C_{4v} <001>   fluoride compensation
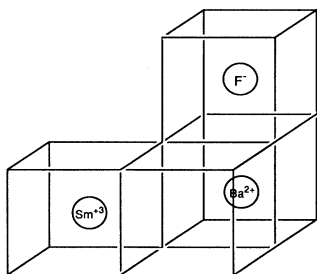
(b) C_{3v} <111>   fluoride compensation

FIG. 5. Model pictures of BaF_2 crystal structure. On each corner of the cube is the fluoride ion. The Sm^{3+} ion substitutes the Ba^{2+} ion when it is doped. It is compensated by the F^- ion in the center of empty cube to form: (a) C_{4v} symmetry when the interstitial F^- ion is in the nearest-neighbor position. (b) C_{3v} symmetry when the interstitial F^- ions is in the next-nearest-neighbor site.

lanthanide series the trigonal compensation of Sm is expected.

It is interesting to consider the nature of the fluorescence transitions of Sm^{2+} in both O_h and C_{3v} centers. Wood and Kaiser[7] found by a Zeeman effect experiment that the two transitions $^5D_0-^7F_1$ and $^5D_0-^7F_3$ belong to the magnetic dipole type. From parity consideration only the A_{1g} emitting state to these two T_{1g} ground states are allowed in a magnetic dipole transition. In the present studies the $^5D_0-^7F_0$ transition did not appear at all, although in Wood and Kaiser's spectrum its intensity was similar to that of the $^5D_0-^7F_3$ transition. The absence of the $^5D_0-^7F_0$ transition from our spectrum agrees with the selection rule for magnetic dipole transitions. Kaiser, Garrett, and Wood[8] reported that their CaF_2 crystal had a concentration of Sm in the range of 0.02 to 1 % and had much trivalent Sm, therefore there was a large concentration of interstitial fluorides. Wood and Kaiser[7] said that the BaF_2 sample had similar concentration of Sm to the CaF_2. Hence it was possible that some of interstitial fluorides might be located near the divalent Sm. These Sm^{2+} ions would display the $^5D_0-^7F_0$ transitions in their spectrum. As seen in our C_{3v} $Sm^{2+}:F^-$ emission spectrum, the $^5D_0-^7F_0$ line is more intense than any of the other $^5D_0-^7F_J$ lines and only a small amount of $Sm^{2+}:F^-$ complex would be needed to explain Wood and Kaiser's observation. It indicates that an electric dipole transition mechanism is involved because the $A_1(^5D_0)-A_1(^7F_0)$ is forbidden in C_{3v} symmetry for a magnetic dipole transition. For the transitions from $^5D_0$ to $^7F_2$ and $^7F_3$ states, we observed three lines

each [see Figs. 3 and 4(b)], which is consistent with the selection rules for electric dipole transitions. If they were magnetic dipole transitions, there would be two and four allowed emission lines occurring for $^7F_2$ and $^7F_3$, respectively. In the spectrum we observed one electric dipole forbidden transition. It is the $A_1(^5D_0)-A_2(^7F_1)$ transition which is over six times weaker than the $A_1(^5D_0)-E(^7F_1)$ line. We therefore assume that the weaker line belongs to a magnetic dipole transition.

C. Fluorescence and photoionization of the $Sm^{2+}:F^-$ complex

We have proved the existence of the $Sm^{2+}:F^-$ complex in Secs. III A and III B. With an extra fluoride ion near the Sm^{2+} ion, there will be an increase in the negative potential. This potential will raise all of the electronic states closer to the conduction band besides the energy-level splitting effect observed in Sec. III B. This potential also lowers the E_g ($4f^5 5d$) excited state towards ground state by an amount of 220 cm^{-1}. The effect of the change of relative energy levels on the emission and photoionization properties of Sm^{+2} will be shown in the following.

Figure 6 shows the measurements of the fluorescence intensity as a function of temperature for both the compensated and the uncompensated Sm^{2+} ion. The more rapid temperature quenching of the fluorescence of the compensated Sm^{2+} ions is shown clearly. The mechanism for the quenching of the emission with increasing temperature in the $BaF_2:Sm$ system has been studied by several groups over the last few decades.[9-11] Bonch-Bruevich and Ovsyankin[10] proposed the existence of an extremely fast nonradiative relaxation channel from the lowest state of the $4f^5 5d$ configuration to the ^7F multiplet of the $4f^6$ configuration. Chase, Payne, and Wilke[11] claimed that a direct nonradiative transition from the $4f^5 5d$ to the ground state would have a negligible influence on the quantum efficiency. This is because nonradiative transition rates decrease very rapidly as the magnitude of the energy gap between the initial and final states increases. Thus, the nonradiative decay rate to the
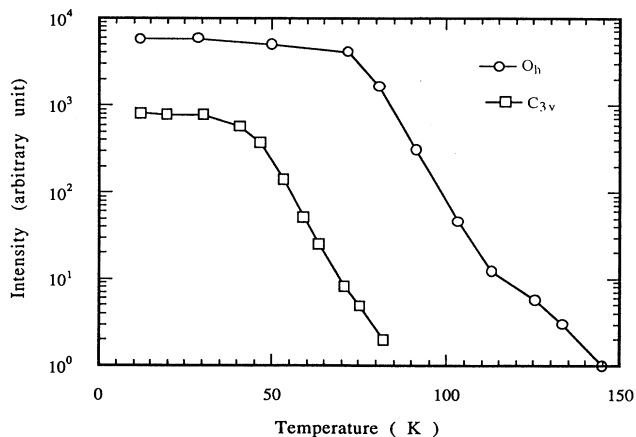

FIG. 6. Measurements of the emission intensity as functions of temperature for Sm^{2+} in both O_h and C_{3v} (with fluoride compensator) sites.

$^5D_0$ excited state must be orders of magnitude larger than that to the ^7F ground term. They concluded that the lowest $4f^55d$ excited state of Sm^{2+} is so close to the conduction band of BaF_2 that the fluorescence intensity is strongly quenched by nonradiative decay due to thermal ionization. They calculated the thermal energy, namely the energy difference between the conduction band and the lowest $4f^55d$ excited state, to be 0.03 eV. Pedrini, Rogemond, and McClure[12] derived this energy gap by using an electrostatic model to be 0.1 eV. Since both values are so small and the first absorption band is quite broad (about 0.25 eV), it led Chase, Payne, and Wilke to think that the lowest $4f^55d$ level of Sm^{2+} may actually be located in the conduction band of BaF_2. The following photoionization experiments will show that excitation to the lowest $4f^55d$ absorption band does not ionize the normal Sm^{2+} but indeed ionizes the Sm^{2+} with F^- compensator.

We did two photoionization experiments on both compensated [experiment (a)] and uncompensated [experiment (b)] Sm^{2+} ions as follows:

(a) At 77 K after creating compensated Sm^{2+}, the absorption spectrum was taken. Then the sample was kept at 77 K and irradiated with a 150-W xenon lamp and filters in the first absorption region. The intensity of exciting light was not recorded. In $\frac{1}{2}$ and 1 h time, two more absorption spectra were recorded. The absorbance of the Sm^{2+} band at 580 nm was reduced to about 60% and 40% of its original value, respectively. The Eu^{2+} absorbance increased correspondingly.

(b) We created uncompensated Sm^{2+} ions at 298 K, then repeated the procedure described in (a) at 298 K. The high temperature only favors the photoionization process. Even for a 2-h irradiation no change in the absorbance of Sm^{2+} was observed on the spectrophotometer.

The results in (a) show that for the compensated Sm^{2+} ion the lowest excited $4f^55d$ state is higher than or degenerate with the conduction band of BaF_2. After excitation the electron will autoionize to the conduction band and become delocalized. Experiment (b) shows that normal Sm^{2+} does not ionize under the same condition.

To find the photoionization energy of uncompensated Sm^{2+}, the sample in experiment (b) was irradiated with 400 nm light matching the second absorption band of Sm^{2+}. At both 77 and 298 K, the photoionization of Sm^{2+} occurred. It can be reasonably assumed that the conduction band of the BaF_2 host is located between the two absorption bands of the uncompensated Sm^{2+}. This means that the compensating fluoride will raise the electronic states of Sm^{2+} at least a quarter of an eV, equal to the bandwidth of the first absorption peak.

In the other experiment, we have also found that the uncompensated Sm^2 ion traps electrons more efficiently than the compensated Sm^{2+} ion does. Before the ionizing irradiation no Sm^{2+} fluorescence was detected, confirming that the fresh sample contains only Sm^{3+}. After 20 min irradiation at 77 K the fluorescence intensity attained its maximum. Only the uncompensated Sm^{2+} fluoresces at that temperature. Further irradiation did not increase the PMT signal that was 12.5 nA as read

from an electrometer. Meanwhile the absorption of Sm^{2+} increased. After annealing the sample to room temperature for a few hours, the fluorescence signal was measured at 77 K again. It was found that the reading of the electrometer jumped to 253 nA. The simple explanation is that the small amount of uncompensated Sm^{3+} is converted to Sm^{2+} very soon upon irradiating while the unstable nonfluorescent $Sm^{2+}:F^-$ complexes accumulate. During annealing at room temperature, the unstable $Sm^{2+}:F^-$ dissociated and produced a large amount of uncompensated Sm^{2+} and a correspondingly large fluorescence signal.

D. Trivalent Eu^{3+} excitation spectroscopy

From the Sm^{2+} absorption and emission spectra we have found how electrons released from Eu^{2+} are trapped at Sm^{3+} during the photoionization process at 77 K and at room temperature. What happened to the Eu^{3+} ions? Electrons are ionized from Eu^{2+} and most of them are trapped at $Sm^{3+}:F^-$ centers. At 77 K the unstable $Sm^{2+}:F^-$ complexes form. We suppose that after losing electrons Eu^{3+} ions will stay in cubic sites until they are compensated locally by fluoride ions. So if we warm the crystal to room temperature the $Sm^{2+}:F^-$ will dissociate and Eu^{3+} will become compensated. The following excitation spectra show that this is what happens.

The 2000-W xenon lamp and single monochromator were used to ionize divalent Eu^{2+} ions at 234 nm and the excitation spectra of the Eu^{3+} in the region of the $^7F_0-^5D_1$ transitions were obtained. The fluorescence is monitored by a R456 photomultiplier behind a double monochromator set at 562 nm corresponding to the $^5D_0-^7F_1$ emission, similar to Sm^{2+} as shown in Fig. 3. All the excitation spectra were done at 77 K. Figure 7(a) is the excitation spectrum of the fresh crystal. Two
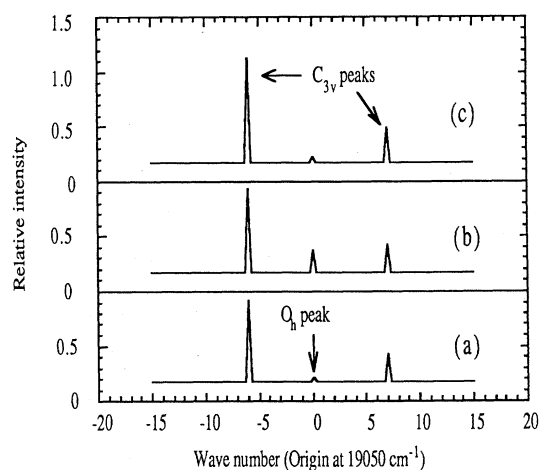

FIG. 7. Excitation spectra of the Eu^{3+} ion in BaF_2:Eu:Sm recorded at 77 K. The central peak at 19065 cm^{-1} involves the $^7F_0-^5D_1$ transition in O_h symmetry. It splits into two peaks at 19059 and 19072 cm^{-1} at lower symmetry (C_{3v}). (a) The spectrum of fresh sample, (b) after irradiated with 233 nm light at 77 K, (c) annealed to room temperature then cooled to 77 K.

prominent peaks (at 19 059 and 19 072 cm^{-1}) due to splitting of the $^5D_1$ level in a C_{3v} crystal field and a little peak (at 19 065 cm^{-1}) between them due to the O_h center were observed. This shows that most of Eu^{3+} were compensated by fluoride ions originally. Figure 7(b) is the excitation spectrum obtained immediately after a photoionization irradiation was done at 77 K. The obvious intensity increase of the central peak indicates the production of cubic Eu^{3+} ions due to photoionization of divalent Eu which were not compensated previously. Figure 7(c) is the spectrum taken after annealing the crystal at room temperature and cooling it back to 77 K. The central peak decreases to its value before irradiation and the C_{3v} lines increase correspondingly. The entire process is consistent with changes in the Sm absorption and emission spectra. Further, it confirms that at 77 K electrons can be ionized from Eu^{2+} and trapped by the Sm^{3+}:F$^-$ centers to form unstable Sm^{2+}:F$^-$ complexes while interstitial fluorides are frozen in their original positions. No unsymmetrical relaxation of the F^- ions takes place. The ionized Eu^{2+} maintains cubic symmetry in the BaF$_2$ lattice.

E. Eu^{2+} Photoionization efficiency

The sample of BaF$_2$ doped with 0.01 mol % of Eu and 0.02 mol % of Sm was used in this experiment.

A 2000-W xenon lamp was used as irradiation source. An H-10 uv single monochromator was used for selecting uv light near the absorption maximum of Eu^{2+} (233 nm with a bandwidth of 8 nm). The sample was put behind a mask which is about 1.5 mm by 0.7 mm. This mask is almost as large as both the images of focused xenon light and the detecting beam of the HP diode array spectrophotometer. The absolute intensity of exciting light was measured by replacing the sample with a thermopile. The irradiation caused ionization of Eu^{2+}. The electrons captured by Sm^{3+} ions created a large amount of Sm^{2+} ions. In the absorption spectrum one can easily find the decrease of the Eu^{2+} peak and increase of the Sm^{2+} peak as irradiation progresses. Finally a photostationary state will be reached where 233-nm light will ionize the accumulated Sm^{2+} ions at the same rate as Eu^{2+} ions.

A singly doped BaF$_2$:Sm 0.02 mol % crystal was reduced by the additive coloration method. The absolute absorbance of Sm^{2+} was taken as the standard value by assuming the nominal concentration is correct. Taking into account the factors of decrease of Eu^{2+} absorption and small overlap of absorption of divalent Eu and Sm at the 233-nm region, we finally plot two ionization curves both at room temperature and 77 K. The y axis represents the number of divalent Sm created and the x axis is the number of photons absorbed by divalent Eu. Assuming every ionized electron is only trapped by a trivalent Sm ion we calculated the ionization efficiency of Eu^{2+} to be 9.7% at 298 K and 6.0% at 77 K. A good linear fit was obtained as shown in Fig. 8.

The same experiment on the same setup was carried out for a SrF$_2$:Eu 0.01%:Sm 0.02% sample to get its ionization efficiency in comparison to the BaF$_2$ sample. It is 9.1 times less efficient in SrF$_2$ than in BaF$_2$ at 300 K or
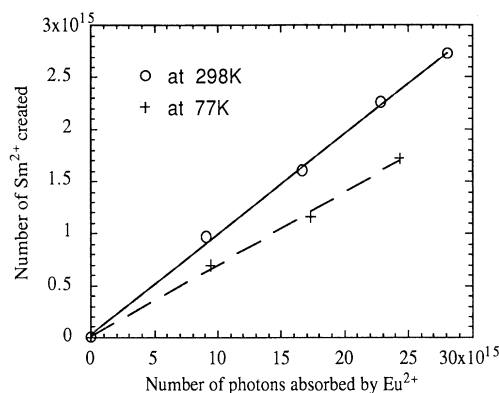

FIG. 8. Plot of the number of divalent samarium atoms formed by irradiation of a BaF$_2$:Eu:Sm crystal vs the total number of photons absorbed by divalent europium at 298 K (solid line) and 77 K (dotted line).

about 1.0%. This agrees well with the ionization efficiency of 1% in SrF$_2$ obtained by Fuller and McClure at 233 nm and 295 K. At 77 K no photoionization in SrF$_2$ was seen by this experiment though more photons were absorbed than in other runs, again in agreement with Fuller and McClure.

The temperature dependence of absolute ionization efficiency in BaF$_2$ and SrF$_2$ differs very much from each other. The magnitude of the photoionization efficiency, i.e., the rate of the forward reaction in Eq. (1), depends primarily on these factors: ionization efficiency of the Eu^{2+} ion, trapping efficiency at the Sm^{3+} ion, geminate recombination rate, and backward reaction rate. The last factor can be ignored in the early stage of the forward reaction. Note that the saturation effect was not seen in Fig. 8. Besides, the originally existing Eu^{3+} ions may also reduce the total efficiency. The ionization of the Eu^{2+} ion should be independent of temperature because it is a fast process, occurring in a short time compared to the thermal relaxation of the excited ion into the lowest excited state. If the electron is ejected with an excess kinetic energy equal to $h\nu - E_0$, where E_0 is the threshold energy, this energy is usually much greater than kT. This excess kinetic energy helps the electron overcome the recombination possibility and put it into the conduction band. The movement of the free electron does not need to be assisted very much by phonons which play an extremely important role in the movement of interstitial fluorides. Hence the electron will be more influenced by the strong Coulomb fields of the donor ion and the traps than by phonons. The ionization efficiency of near 10% at room temperature and 6% at 77 K in the BaF$_2$ host shows the weak temperature dependence of both the ionizing and the trapping process. Further, 10% is a rough estimate of the ratio of trapping and recombination rates for our sample if the original amount of Eu^{3+} ions can be ignored. Then why in SrF$_2$ is the ionization efficiency at 77 K over 1000 times less than that at room temperature? It is reasonable to assume that the ionization process is almost temperature independent in SrF$_2$ and BaF$_2$. However, the structure of the trapping center is different in

these two hosts, namely, C_{4v} in SrF_2 and C_{3v} in BaF_2 (see Fig. 6). In the C_{3v} center, interstitial fluoride is sitting at 0.86 times the lattice constant from the Sm^{3+} ion while it is 0.5 lattice constant away in the C_{4v} center. Besides, the lattice constant is smaller for the SrF_2 crystal. Clearly the C_{4v} Sm^{3+}:F^- forms a tight and stable dipole in SrF_2 which gives rise to only a small attractive Coulomb force towards a nearby electron. The electron may need assistance of lattice vibration to fall onto the Sm^{3+} ion. That makes the trapping process an activated one in the range of from 300 to 200 K in SrF_2 as measured by Fuller and McClure. From the absorption spectrum Fig. 1(d) it is also noticed that the unexpected impurity, Ce^{3+}, is not an efficient trap in comparison to Sm^{3+}, even though it is probably C_{3v} compensated, according to Ref. 4. The probable reason is that the ground state of Ce^{2+} is $4f5d$ in contrast to Sm^{3+} in which all electrons in the ground state are in $4f$ orbitals. The $4f$ orbitals are confined close to the ion whereas the $5d$ orbitals extend appreciably into the lattice. Hence the ground state of Ce^{2+} will be destabilized by the strong interaction between the $5d$ valence electron and fluoride compensator if an electron is trapped by Ce^{3+}.

IV. CONCLUSIONS

In this paper we have found how the interstitial fluorides influence electron trapping for a well-known photoreaction in doubly doped crystals. The entire process can be described as follows: In BaF_2:Eu:Sm crystal, when Eu^{2+} absorbs the uv light at about 233 nm wavelength, its valence electron is ionized to enter the conduction band of the host. The free electron will be trapped by any nearby trivalent impurities. It was found that the uncompensated trivalent Sm ion acts as a better trap than the fluoride compensated Sm^{3+} ion which has the dominant concentration. The Ce^{3+} ion is a much less efficient trap than the Sm^{3+} ion in BaF_2. When the free electron approaches the compensated Sm^{3+}:F^- complex, the Sm^{+3} ion will trap it to form an unstable Sm^{2+}:F^- complex which exists only at low temperature (e.g., 77 K) and dissociates at room temperature with the fluoride compensator diffusing away. The free interstitial fluoride is finally trapped by the trivalent Eu ion which prefers to be compensated after donating an electron.

With a fluoride interstitial compensator, Sm^{2+} ions feature different absorption and emission spectra from the normally observed ones. The photoionization threshold of Sm^{2+} ion was lowered by more than a quarter of an eV by its negative charge compensator. The analysis of the emission spectrum led to the conclusions that the Sm^{2+}:F^- complex is of C_{3v} symmetry and transitions become electric dipole allowed in contrast to magnetic dipole transitions in the O_h symmetry Sm^{2+} ion.

ACKNOWLEDGMENTS

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