Irradiation Damage in SrF_2 and BaF_2^+

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The thermoluminescence of rare-earth-doped SrF2 and BaF2 irradiated with x rays at 77°K is interpreted in terms of the appearance and disappearance of three paramagnetic hole centers. The V_K center is similar to one previously reported in CaF₂. The V_K' center appears to be a V_K center trapped near a monovalent impurity ion. The third center, designated as V_H , is associated with an interstitial fluorine. Separate thermal activation of translational and rotational motion has been observed for the V_K center in BaF₂.

I. INTRODUCTION

▶ RYSTALS of CaF₂, SrF₂, and BaF₂, doped with rare-earth trifluoride, can be grown with trivalent rare-earth ions substituting for the divalent cation and with charge compensation via an interstitial Ffluorine ion. Electron-spin-resonance measurements¹ show that in the cubic alkaline-earth-fluoride hosts the trivalent rare-earth ion is often found in a variety of different local symmetries. If the compensating F⁻ ion is far from the trivalent rare-earth ion (Re³⁺), one finds the Re³⁺ in cubic symmetry. Otherwise, one observes one or another form of axial symmetry. It is known that x rays induce reduction of trivalent rareearth ions to the divalent state.² If the crystal is heated from the irradiation temperature of 77 up to 450°K, thermoluminescence glow peaks appear at different temperatures,²⁻⁵ and the rare-earth ions return to the trivalent form. Thermal activation of various hole traps was proposed² in order to explain the existence of these glow peaks. The aim of the present work is to provide further proof that this is indeed so for SrF₂ and BaF_2 and to demonstrate some of the differences between the various hole traps.

According to this previous model, holes thermally activated from the various hole traps recombine with the divalent rare-earth ion (Re^{2+}) to form an excited state of Re³⁺. The radiation that accompanies the decay of this excited state is responsible for the thermoluminescence. It has been shown that the spectrum of the thermoluminescent emission is characteristic of the

Re³⁺. Although this model required that one postulate a number of different types of hole traps in order to explain the several thermoluminescent glow peaks, the only clear identification of a paramagnetic hole center in these materials was the self-trapped $V_{\mathcal{K}}$ center in $CaF_{2.6}$ Holes in the narrow $F^{-}p$ band of these alkalineearth fluorides become self-trapped through the action of neighboring fluorine atoms moving together to form a localized trap that resembles an F_2 -molecule. This decays at 138°K and does coincide with the temperature of one major glow peak in CaF₂.

The present investigation identifies three different paramagnetic hole centers and associates them with three different glow peaks. In SrF2 and BaF2, we found that upon x irradiation at 77°K, V_K centers are produced together with divalent rare-earth ions. As a result of the thermal activation of this self-trapped hole, one observes thermoluminescent emission along with the appearance of two other paramagnetic hole centers. This is shown in Fig. 1(a). One of them, designated V_H , is associated with an interstitial fluorine and is oriented in the [111] direction. As is the case for the V_K center, the V_H center has the form of a F_2^- molecule. When this center is thermally activated at a different temperature, it too results in a glow peak. The second center, designated V_{κ}' , also represents a trapped hole in the lattice oriented in the $\lceil 100 \rceil$ direction. This hole, however, is trapped by a local negative charge, most probably a monovalent positive ion substituting for the divalent cation. Thermal activation of this center results in still another glow peak.

In the case of BaF_2 , it was possible to resolve two separate glow peaks at two different temperatures that could be associated with thermal activation of the V_K center. As we will discuss below, by orienting the V_K centers with polarized uv light, we were able to associate one of these with thermal activation of the V_K center along its axis (motion along the [100] axis of its orientation) and motion in which the orientation is not preserved.

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¹ M. J. Weber and R. W. Bierig, Phys. Rev. 134, A1492 (1964). A detailed account of previous work is quoted.

² J. L. Mertz and P. S. Pershan, Phys. Rev. 162, 217 (1967); 162, 235 (1967); in *Optical Properties of Ions in Crystals*, edited by Crosswhite and Moos (Wiley-Interscience, Inc., New York, 1967), p. 117; J. L. Mertz, Ph.D. thesis, Harvard University, 1966 (unpublished).

⁸V. A. Arkhangelskays, Opt. i Spektroskopiya 16, 628 (1964) [English transl.: Opt. Spectry 16, 343 (1964)]; Izv. Akad. Nauk SSSR, Ser. Fiz. 29, 454 (1965) [English transl.: Bull. Acad. Sci. USSR, Phys. Ser. 29, 465 (1965)

⁴ M. Schlesinger and P. W. Whippey, Phys. Rev. 162, 268 (1967).

⁵ A. Tzalmona and P. S. Pershan, Appl. Phys. Letters 13, 262 (1968).

⁶ W. Hayes and J. W. Twidell, Proc. Phys. Soc. (London) 79, 1295 (1962); in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 1, p. 163.

Crystal	Center	gu	gı	A (g)	<i>B</i> (g)	A'(g)	B'(g)	Angle (°)	Decay temp. (°K)	F-F distance (Å)
LiF	$V_{F}^{\mathbf{a}}$ $V_{F}^{\mathbf{b}}$ $H^{\mathbf{o}}$	2.003 ± 0.001 2.001 ± 0.002 2.001	$\begin{array}{c} 2.023 {\pm} 0.001 \\ 2.023 {\pm} 0.002 \\ 2.012 \ / \ 2.014 \end{array}$	887 ± 1 915 ± 1 956	59 ± 1 56 ± 10 -0	 89.8	 24/26	 4.2±0.5	120 230 130	2.84
CaF2	$(1,1,1) \operatorname{defect^{d}}_{V_{F}^{e}}$	2.0017 2.001 ± 0.001 2.002 ± 0.002	2.0105 2.020 ± 0.001 2.019 ± 0.002	1005.9 ± 0.1 899.9 ± 1 916 ± 1	$ \begin{array}{r} 19 \pm 5 \\ 48.5 \pm 2 \\ 45 \pm 10 \end{array} $	15.1 ± 0.3 13.2 ± 0.5	$\leq 4 \leq 4$	 1.7±0.5	60 138 330	2.725
BaF2	$V_K V_K' V_H$	2.000 ± 0.002 2.002 ± 0.002 2.006 ± 0.004	2.020 ± 0.002 2.020 ± 0.002 2.023 ± 0.005	889 ± 2 914 ± 2 864 ± 5	$\begin{array}{rrrr} 46 & \pm 2 \\ 46 & \pm 5 \\ 170 & \pm 30 \end{array}$	•••	•••	… ≤0.5	140 260 180	3.09 2.68
SrF_2	$ \begin{array}{c} V_{\kappa} \\ V_{\kappa'} \\ V_{H} \end{array} $	2.002 ± 0.002 2.000 ± 0.002 2.004 ± 0.005	2.020 ± 0.002 2.020 ± 0.002 2.022 ± 0.005	899 ± 2 914 ± 2 864 ± 5	$\begin{array}{ccc} 47 & \pm 3 \\ 50 & \pm 10 \\ 170 & \pm 30 \end{array}$	$\begin{array}{c} 6.3 \pm 0.2 \\ 5.7 \pm 0.2 \\ 18 \ \pm 2 \end{array}$	•••• •••	≤0.5	160 240 240	2.93 2.54

TABLE I. Data on color centers in LiF and CaF₂ from the literature and on BaF₂ and SrF₂ from the present work.

^a T. O. Woodruff and W. Kanzig, J. Phys. Chem. Solids 5, 268 (1957).
 ^b Reference 9.
 ^e Reference 7.

II. EXPERIMENTAL RESULTS

A. Thermoluminescence and Paramagnetic Hole Centers in BaF₂

We have examined two samples, $BaF_2:Tm(0.02\%)$ and $BaF_2:Dy(0.05\%)$ and a third sample free from rare earths.⁵ After x irradiation at 77°K, the EPR spectrum of an oriented single crystal was measured at 35 Gc/sec. We found at 80°K a V_K center similar to that reported in CaF₂.⁶ The spin Hamiltonian

$$5C = \beta g_{11} S_z H_z + \beta g_1 (S_x H_x + S_y H_y) + A I_z S_z + B (I_x S_x + I_y S_y) \quad (1)$$

for this paramagnetic center has axial symmetry, where the z axis is one of the (100) directions. This Hamiltonian describes the hyperfine interaction with two fluorine nuclei; $I = I_1 + I_2$, where $I_1 = I_2 = \frac{1}{2}$ is the spin of the fluorine nuclei. The constants A and B are a measure of this interaction. The spin of the hole center is $S=\frac{1}{2}$. The measured parameters are listed in Table I. The V_K center has the form of an F_2^- molecule oriented in one of the three equivalent (100) directions in the cubic host. The g_{11} and g_1 of this center, as well as the hyperfine constants A and B, are very close to the corresponding parameters in CaF_2 (see Table I).⁶ The main difference between the self-trapped holes in BaF_2 and CaF_2 is the absence in the former of a measurable hyperfine splitting with two more-distant fluorines. This is expected, since the lattice constant is larger for BaF₂ than for CaF₂. Between 80 and 140°K this center is thermally activated, and two different paramagnetic hole centers appear as well as two glow peaks. We shall prove that one of the centers, designated V_H , is associated with an interstitial fluorine.

In alkali halides, the paramagnetic hole center associated with an interstitial atom (H center) is believed to be the direct product of the damaging irradiation.⁷ In alkaline-earth fluorides, such a center

^d Y. Hou Chu and R. L. Micher, Phys. Rev. Letters **20**, 1289 (1968). • Reference 6. f Reference 8.

 $(V_H \text{ center})$ is formed from the thermally activated V_K center. The angular variation of the EPR spectrum, when the static magnetic field is rotated in the (110) plane, shows that the V_H center represents an F_2^-



FIG. 1. (a) EPR signal intensity is plotted versus temperature for the three paramagnetic centers in BaF₂.Tm(0.02%). A similar curve is found also in BaF₂:Dy(0.05%). (b) EPR signal intensity is plotted versus temperature for BaF₂ free from rare earth; this signal is about two orders of magnitude less than the rare-earth-doped BaF₂. (c) The solid curve is the light intensity of thermoluminescence as a function of the temperature. The *x* points indicate the fraction of the EPR signal in a certain (100) direction which it is possible to orient by polarized uv light (righthand scale) as a function of temperature.

⁷ W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 20 (1959).





FIG. 2. Model for the V_K and V_H centers in MeF₂ host (Me=Ba, Sr, Ca). Full dots are for F^- ; open dots are for the F₂⁻ molecule

molecule oriented along one of the four (111) directions in the crystal (see Fig. 2). When the magnetic field approaches the [100] direction, there are four spectra which coalesce into one. The spin Hamiltonian (1) describes this center if the z axis is now taken to be one of the four directions, and the parameters are given in Table I. The most likely identification of this center is a hole trapped by an interstitial fluorine which compensates the Re³⁺ ion. In rare-earth-free BaF₂, this center is not found [see Fig. 1(b)], since there are no interstitial fluorines. We have examined a BaF₂ crystal doped with both Tm(0.01%) and Na(0.05%). In this case, the Tm³⁺ is overcompensated by Na⁺, which is substituted for Ba⁺⁺. Only traces of V_H centers are found in this case. The values of the hyperfine splitting constants for the V_H center is more isotropic [i.e., |A+2B|/|A-B| for V_H is greater than for V_K].

The spin-lattice relaxation for the V_H center is characterized by a much shorter T_1 than for the V_K center, since at 80°K, saturation of the V_H center requires about 20 dB more power than saturation of the other hole centers. Figure 2 shows a model for the V_K and V_H centers. We suggest that the faster relaxation rate of the V_H center could be caused by a tunneling mechanism between the different possible orientations of the V_H center. For example, the interstitial fluorine atom may hop between the 8 fluorines at the apexes of the cube (see Fig. 2). The relaxation is the same for both BaF₂:Tm and BaF₂:Dv samples. In fact, it was the fact that the EPR signal associated with the other hole centers could be saturated at modest powers that made it possible to isolate the spectrum of the V_H center.

The second hole center that appears when the V_K center disappears is designated $V_{K'}$ [see Fig. 1(a)]. This center has tetragonal symmetry, and it is very similar to the V_K center. It is oriented along the [100] direction, and it is not thermally activated until one reaches a higher temperature, 260°K. The higher value of the hyperfine constant A might arise if the hole is trapped by a local negative charge in the crystal such as Na⁺ substituting for Ba⁺⁺ or Ba⁺⁺ vacancies (V_F centers).^{8,9} The possibility that a monovalent ion traps

this hole is not at all unlikely. For example, in BaF_2 : Tm:Na, traces of V_{K} center are found directly after irradiation at 80°K. Analysis of all of our crystals by Jarrel and Ash Co., Waltham, Mass., show the presence of monovalent ions such as Ag, Na, and Cu. We have not observed the deviations from axial symmetry for the V_{K} center in BaF₂ that appeared for the V_{F} center in CaF_2 (see Table I).⁸

Optical absorption measurements^{2,10} show that the V_K center absorbs between 340-360 m μ . No optical band has been found for the V_H center. This is similar to the case in LiF, where the absorption band for the V_H center is also not observed.⁷

Optical absorption measurements were made on BaF₂:Tm and for rare-earth-free BaF₂. The absorption is believed to result from an electronic transition between the ground state $({}^{2}\Sigma_{u}^{+})$ and the excited state $({}^{2}\Sigma_{g}^{+})$ of the F_{2}^{-} molecular ion.¹⁰ This transition is strongly polarized (σ bond). Consequently, it is very easy to orient the V_{κ}' centers by polarized uv light.¹¹ We have illuminated the crystal with polarized uv light so that the plane of polarization is perpendicular to one of the $\langle 100 \rangle$ crystal directions. After illumination of the sample at a given temperature, the crystal is cooled down to liquid-nitrogen temperature. The time needed to establish thermal equilibrium is estimated to be 1–2 sec. The EPR spectrum is measured at 80°K. If the sample is illuminated at 77°K, the number of the centers in the $\langle 100 \rangle$ direction parallel to the polarization of the uv light is decreased down to 20% of its original value [see Fig. 1(c)]. The number of the centers in the other two $\langle 100 \rangle$ directions is increased accordingly. If the sample is kept immersed in liquid nitrogen, the unequal distribution of the V_{κ} centers is preserved at least for 24 h. If the illumination experiment is done between 120 and 140°K, the fraction of the centers oriented by the uv light varies according to Fig. 1(c). In the temperature range from 80 up to 120°K, although the total number of V_K centers decreases, the ratio of centers in two different $\langle 100 \rangle$ directions remains the same (as a result of the uv illumination). This clearly indicates that below about 120°K, motion is possible which *does not* involve any reorientation.

In more detail, the interpretation is as follows: At approximately 100°K, the self-trapped V_K center becomes thermally activated in the sense that it can diffuse parallel to the [100] direction in which it is oriented. Presumably the potential barrier for reorientation, to (say) the [010] direction, is too high, and this type of motion does not occur. Although the hole is now said to be free for motion in one dimension, it is most likely that this motion is, in fact, limited by

⁸ J. Sierro, Phys. Rev. 138, A648 (1965).

⁹ W. Kanzig, J. Phys. Chem. Solids 17, 80 (1960). ¹⁰ J. M. Beaumont, W. Hayes, G. T. Summers, and J. W. Twidell, Solid State Commun. (to be published). ¹¹ F. J. Keller and R. B. Murray, Phys. Rev. Letters 15, 198 (1965); Phys. Rev. 150, 670 (1966).

1.0

0.8

0.6

0.4

Signal

inhomogeneous local strains or local electric field variations, both of which could arise from the stochastic nature of the impurity distribution. Thus, although the center can diffuse over some distances, its motion is in fact limited, and there is some possibility that the moving hole will not find a new trap with which to combine. At approximately 130°K, however, we argue that thermal activation for reorientation of the V_K becomes possible. Above 130° K, the V_{K} center can diffuse in all three directions, and a complete anneal of this center is accomplished. This experiment has been done with both V_K and $V_{K'}$ centers and with the $V_{K'}$ center alone. The V_K and V_H centers could be easily annealed by heating the crystal above 180°K and keeping the temperature below 260°K. Both V_K and V_{κ}' centers have the same orientational properties. Above 140°K, orientation was not possible for the V_{K}' center. The V_H center could not be oriented at any temperature.

B. Thermoluminescence and Paramagnetic Hole Centers in SrF₂

The behavior of SrF_2 doped with rare earths is analogous to the behavior of BaF₂. The same three paramagnetic hole centers are observed (see Fig. 3). The parameters of the V_K , V_K' , and V_H centers are given in Table I. The thermal activation temperatures are different from BaF_2 as shown in Fig. 3. The data are taken from SrF_2 :Tm(0.02%) and SrF_2 -Dy(0.05%). A rare-earth-free crystal was also examined. Angular variation of the EPR spectrum was taken from crystals oriented in the $\lceil 110 \rceil$ direction, and the magnetic field was rotated in this plane. Perturbation theory¹² was used to analyze the spectra. Since the electron-spinresonance measurements are done at 35 Gc/sec, the perturbation expansion, up to second order, is sufficient. The hyperfine interaction is of the order of 1 kG and $g\simeq 2$ corresponds to magnetic field of 12.4 kG.

Since the lattice constant of SrF_2 is less than for BaF2, the paramagnetic hole centers show additional hyperfine interaction with more-distant fluorines. This is similar for the CaF_2 case. The Hamiltonian is

$$\mathfrak{K} = \beta g_{11} S_z H_z + \beta g_1 (S_x H_x + S_y H_y) + A (I_z S_x + I_y S_y) + A' I_z' S_z + B' (I_x' S_x + I_y' S_y).$$
(2)

For the V_{κ} and $V_{\kappa'}$ centers, I'=1 or 1; the hole spends some time on two more fluorines, each nucleus of which has a spin of $\frac{1}{2}$. For the V_H center aligned along the [111] direction, $I' = \frac{1}{2}$. The hyperfine interaction is most probably due to interaction between the hole wave function with the fluorine nucleus at the apex of the cube opposite the F_2^- molecule (see Fig. 2). The V_H center could be well observed only at 80°K because of relaxation broadening at higher temperature. In BaF₂, the V_H center has a width smaller than 10 G.

EPR 0.2 of the 1.0 ٧_ĸ Intensity (b) 0.8 0.6 V¹_K 0.4 0.2 Centers 0 (c) .0-5* Р ¥ Light Intensity Oriented ď Praction 80 120 160 200_ 240 280 (°K) FIG. 3. (a) EPR signal intensity in plotted versus temperature for the three paramagnetic centers in SrF₂:Tm(0.02%). A similar curve is found also in SrF₂:Dy(0.05%). (b) EPR signal intensity is plotted versus temperature for SrF₂ free from rare earth; this signal is about two orders of magnitude less than the rare-earthdoped SrF_2 . (c) The solid curve is the light intensity of thermo-

In this case, there was no appreciable broadening up to the annealing temperature of this center. Assuming that the hopping of the V_H center in SrF_2 determines the relaxation time,¹³ we have

luminescence as a function of the temperature. The x points indicate the fraction of the EPR signal in a certain (100) direction

which it is possible to orient by polarized uv light (right-hand scale) as a function of temperature.

$$1/T_1 = 1/T_2 \sim e^{-E/\Delta kT}$$
, (3)

where $\Delta f = \pi T_2^{-1}$ is the width of the line. At 80°K, $\Delta f = 8$ G, and at 240°K, $\Delta f = 160$ G. The estimated activation energy is 0.0031 eV (250 cm⁻¹).

C. Thermoluminescence and Paramagnetic Hole Centers in CaF₂

The V_K center was first observed⁶ in CaF₂. This center is thermally activated between 120 and 150°K (see Fig. 4). The thermoluminescence was intensely studied in this host. Six glow peaks are found in the temperature range from 80 up to 450°K. The rotational properties of the $V_{\mathcal{K}}$ center have been studied (see Fig. 4) by polarized uv light and by measuring the EPR spectra of the holes. Up to the temperature of



¹² B. Bleaney, Phil. Mag. 42, 441 (1951).

¹³ S. Alexander and A. Tzalmona, Phys. Rev. Letters 13, 546 (1964); Phys. Rev. 138, A845 (1965).



FIG. 4. EPR signal intensity of the V_K center is plotted versus temperature in CaF₂:La(0.1%). The x points indicate the fraction of the EPR signal in a certain (100) direction, which is possible to orient by polarized uv light (right-hand scale) as a function of temperature.

disappearance of the V_{κ} center, it is possible to orient, by uv polarized light, about 80% of the centers. No V_{κ}' centers are present in CaF₂. In some cases, the annealing temperature of the V_K center (CaF₂:La 0.01%) is as low as 80°K. A very complex spectrum with $g \simeq 2$ is present. Most of the centers are probably oriented along the $\lceil 110 \rceil$ direction, and some of them along the [111] direction.¹⁰ However, the complexity of the spectrum does not allow any reliable measurements. It is obvious that the next near neighbors of fluorines are observable, and the hyperfine interaction is extremely complex.

We have examined a sample grown as "pure" CaF₂. The EPR shows Gd³⁺ only in cubic sites at concentrations of about 10⁻⁶. Irradiation by x rays at 77°K causes complete disappearance of this spectrum and conversion to Gd^{2+} . Figure 5 shows that the total intensity of glow peaks as a function of the temperature corresponds to the intensity of the Gd³⁺ which reappears. If one illuminates the sample, irradiated at 77° K by x rays, with visible light, the V_K centers disappear (the sample is left at 77°K), and part of the Gd³⁺ spectrum reappears.¹⁴ It should be pointed out that irradiation at room temperature by x rays results in Gd³⁺ in symmetry lower than axial and a very broad line (1200 G) centered at about $g \simeq 2.1$.

We have examined $CaF_2:Lu(0.1\%)$. After x-raying at 77°K, we observed a spectrum which is probably produced by Lu^{++} ions¹⁵ and V_K centers.

D. High-Resolution Thermoluminescence Spectra of Gd^{3+} in SrF_2 and BaF_2

The symmetry of the trivalent rare-earth ion, which participates in the charge conversion process, can be determined by measuring the high-resolution spectra of the thermoluminescence and by EPR. The spectroscopy of Gd³⁺ in crystal-field environment is well

understood, since data are available from fluorescence excited by x rays,¹⁶ fluorescence excited by uv,¹⁷ and some previous thermoluminescence studies.³ EPR data are also available¹⁸ for Gd³⁺ in various symmetries. However, it is very difficult to observe and measure the paramagnetic hole centers when the host is doped with Gd³⁺. In most cases, the efficiency of the charge conversion by x rays is quite low. The intensity of the EPR spectra of Gd³⁺ before and after the irradiation seems to be unchanged. (The sample mentioned in Sec. II C was of very low concentration.) The efficiency of the charge conversion is estimated to be no more than 2-3% for doping concentrations of Gd³⁺ in the range of 0.01-0.05%. Our rough measurements of the EPR spectra of Gd³⁺ in both SrF₂ and BaF₂ give results similar to those reported by Sierro.¹⁸ In BaF₂, we find spectra arising mainly from ions in sites of trigonal symmetry, but there are also present signals from ions in cubic sites. In both cases, the zero-field splitting is identical with the Sierro¹⁸ results: 0.291 cm^{-1} for the trigonal sites and 0.116 cm^{-1} for the cubic sites. In BaF₂, it is most likely that the trigonal sym-



FIG. 5. The solid curve represents the total integrated intensity of thermoluminescence of CaF₂:Gd, irradiated by x rays at 77° K, as a function of temperature; EPR shows that the Gd³⁺ ion is only in cubic sites. The x points represent the EPR intensity of Ge^{3+} as a function of temperature.

¹⁴ Z. J. Kiss and D. L. Staebler, Phys. Rev. Letters 14, 691 (1965). ¹⁵ A. Tzalmona and P. S. Pershan (to be published).

¹⁶ J. Makovsky, in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book

Co., New York, 1960); J. Chem. Phys. 46, 390 (1967). ¹⁷ F. Z. Gilfanov, Zh. S. Dobkina, A. L. Stolov, and L. D. Livanoca, Opt. i Spektroskopiya 20, 283 (1966) [English transl.: Opt. Spectry (USSR) 20, 152 (1966)]. ¹⁸ J. Sierro, Phys. Letters 4, 178 (1963).



FIG. 6. (a) Thermoluminescence spectrum of Gd^{3+} in BaF_2 below 160°K; this is a ${}^{6}P_{7/2}$ to ${}^{8}S_{7/2}$ transition. (b) Thermoluminescence spectrum of Gd^{3+} in BaF_2 above 160°K [the same transition as in (a)].

metry of the rare earth is given by an interstitial fluorine in the [111] direction. The zero-field splitting of the ${}^{8}S_{7/2}$ level is small compared to the zero-field splitting of the order of 2 cm⁻¹ observed in CaF₂ and SrF₂, when O₂⁻ compensation is purposely introduced in the crystal to create trigonal symmetry.

Figure 6 shows the thermoluminescence spectra of Gd^{3+} at two different temperature ranges. Below 160°K, recombination occurs with ions in trigonal symmetry. This is evident by the four-peak structure of the thermoluminescent spectrum which corresponds to electronic transition between the four Kramer's doublets which result from the ${}^{6}P_{7/2}$ level in an axial crystal field and the ground level. Above 160°K, the recombination occurs at cubic sites, and these result in only three peaks.

The different symmetries observed in thermoluminescence can be understood on the basis of the following model: A cubic Gd^{2+} represents a neutral charged hole trap in the BaF₂ lattice. A Gd^{2+} -F⁻ pair is negative. At lowest temperatures, a thermally activated hole will most probably be attracted to the negative defect, and the low-temperature thermoluminescence will be dominated by this center. As these fill up at higher temperatures, the neutral cubic Gd^{2+} will become important and will, in turn, dominate the emission spectra.

In SrF₂, the situation is more complicated. EPR spectra show that trigonal, tetragonal, and cubic symmetry are all present.¹⁸ The low-symmetry high-resolution spectra could be tetragonal or trigonal. The splitting is due to the splitting of the excited state ${}^{6}P_{7/2}$ since the ground-state splitting, according to the EPR data of ${}^{8}S_{7/2}$, is not resolved. The $J = \frac{7}{2}$ level splits

in cubic symmetry into a Γ_6 , Γ_7 , and Γ_8 , whereas, in lower symmetry there are four Kramer doublets. If one compares the lives assigned by Makovsky,¹⁶ our spectra are closer to the trigonal assignment than to the tetragonal one. The details of our results are given in Table II.

III. EXPERIMENTAL TECHNIQUE

The electron-spin-resonance data are taken with Varian V-4500 35-Gc/sec spectrometer. A special attachment has been built to allow both x irradiation and the collection of EPR data, keeping the sample at 77°K. Figure 7 shows the attachment which consists of a quartz Dewar with two suprasil quartz windows, each 0.020 in. thick. This window combination transmits 35% of the x-ray beam and did not darken after many hours of irradiation.² X-ray exposures are made



FIG. 7. Quartz liquid-nitrogen Dewar with the bottom part of the 35-Gc/sec cavity supported by springs. This attachment allows us to irradiate the sample at 77°K and measure the EPR spectra without heating the sample. This Dewar is used also to measure the uv thermoluminescence spectra of Gd^{s+} and to illuminate the sample with polarized uv light.

TABLE II. Thermoluminescence of Gd^{3+} (${}^{6}P_{7/2}$ - ${}^{8}S_{7/2}$ transitions). The low-temperature spectrum for Gd^{3+} in SrF₂ (column 3) is measured at 77°K and assigned to trigonal sites. The high-temperature spectrum (column 3) is assigned to cubic sites. The low- and high-temperature spectra for Gd^{3+} in BaF₂ (column 3) is measured at 300°K. The accuracy of the thermoluminescence spectra is ± 4 cm⁻¹.

	Lo	ow-tempe spectru	rature	High-temperature spectrum				
	(Å)	(cm ⁻¹)	(cm ⁻¹) a	(Å)	(cm-1)	(cm ⁻¹) a		
SrF_2	3116.5	32 087	32 076.3	3111.6	32 082	32 095.1		
	3114.2	32 111	32 081.8	3113.7	32 116	32 107.9		
	3113.6	32 117	32 103.6	3110.4	32 150	32 142.9		
	3110.5	32 149	32 137.2					
BaF₂	3111.7	32 137	32 129.1 ^ь	3111.8	32 136	32 142ь		
	3110.4	32 150)	20.140.7	3109.7	32 157	32 154		
	3109.6	32 158)	32 149.7	3106.9	32 186	32 184		
	3106.6	32 190	32 176.0					
a Ref	ference 16		^b Reference	ce 17.				

Kelefence 10. Kelefence 17

with a molybdenum x-ray tube powered by a General Electric supply operated at 50 kV and 20 mA. The bottom part of the 35-Gc/sec cavity and the cold finger are supported by springs. The sample is at the level of the window during the x-ray exposure or the illumination with polarized uv light. The irradiation exposures are made separately from the EPR spectrometer. After the irradiation, the cavity and the wave guide with the iris is screwed up into the bottom part of the cavity. They are pushed down so the sample sits on the middle of the 8-in. pole pieces of the Harvey-Wells Nuclear Corp. magnet. The sample temperature is measured by a copper-constantan thermocouple (made from 30-gauge wire) with the reference junction in icewater. The thermocouple junction is pressed with tape to the bottom part of the cavity, as close to the sample as possible. The static magnetic field is measured by a free precision NMR signal with spin-echotype apparatus.

Marginal oscillators, usually used to measure the magnetic field, turn out to be not sensitive enough in our case. The reason is the inhomogeneous broadening of the NMR line due to the inhomogeneous magnetic field. We have 8-in. tapered pole pieces and a 2-in. gap. The maximum field is 17 kG. The NMR probe sits on $2-2\frac{1}{2}$ in. from the center of the pole pieces of the magnets. It should be pointed out that the sample in the liquid-nitrogen Dewar is in a homogeneous magnetic field in the middle of the pole pieces. A modified version of a single-coil spin-echo-type system, described elsewhere¹³ is used. It is operable from 2-22 Mc sec. The higher magnetic fields are measured by deuterium resonance (D_2O sample), whereas the lower fields are measured by proton probe (mineral oil). An X-Y recorder is used with the EPR spectrometer (Mosley 7000 Å). The X is driven by the same potentiometer as drives the current of the magnet.

The absorption measurements are done in a Cary 14 in a liquid-nitrogen Dewar with a window of 0.020-

in. suprasil quartz for x-ray exposure. The uv polarizedlight experiment is done by a 160-W uv source, a quartz lens, a Corning 7-54 filter, and a Polaroid uv polarizer. The low-resolution thermoluminescence measurements are done in the same Dewar (Fig. 7) as the EPR measurements. We used EMI 6255B photomultiplier operated at 1200 V. The high-resolution thermoluminescence spectra are taken with Jarrel and Ash 1-m spectrometer, model 78-420. We used a 9558QA photomultiplier to measure the high-resolution spectrum of Gd³⁺ around 3100 Å lines. Different temperatures in our Dewar setup are obtained by allowing the liquid nitrogen to evaporate. It takes about 12 h to go from 77°K to room temperature. The SrF₂ and BaF₂ samples are purchased from Optovac, Inc. The CaF₂ samples are grown in this laboratory by the Bridgman-Stockbarger technique. The size of the sample is $1.5 \times 1.5 \times 3$ mm for EPR purposes and $10 \times 10 \times 6$ mm for thermoluminescence measurements.

IV. DISCUSSION

The experimental results presented in Sec. II tend to confirm the previous hypothesis that thermal activation of various hole traps is responsible for the observed thermoluminescence and re-oxidation ($\text{Re}^{2+} \rightarrow$ Re^{3+}) observed in BaF₂:SrF₂ (and implicitly in CaF₂) doped with rare-earth ions and then subjected to ionizing radiation at 77°K.

The trivalent rare earth in the alkaline-earth-fluorine host acts as a trap for an electron which is excited from the valence band into the conduction band. The missing electron in the F⁻ valence band polarizes the lattice, and as a result, a self-trapped hole is formed.⁶ The present work confirms this phenomenon (shown previously ⁷ in alkali halides) for the alkaline-earth fluorides. Two fluorines are pulled together to form an F₂molecule (see Fig. 2). The self-trapped hole, thermally activated at certain temperatures, could be trapped either by an interstitial fluorine which compensates the Re³⁺ and forms a V_H center; an effective negative charge such as a monovalent ion substituting for the divalent cation and a V_{K}' center is formed; or a Re²⁺, in which case recombination occurs and a glow peak appears. In BaF₂, the potential barrier to be crossed for linear motion is probably lower than the potential barrier for rotational motion.

In BaF₂, it appears that the V_H and V_K' are thermally activated at different temperatures, and one observes two different glow peaks between 140°K and room temperature. This does not appear to be the case in SrF₂, and only one glow peak is observed for which the V_K' and the V_H centers both disappear. In both SrF₂ and BaF₂, a faint thermoluminescence is observed up to 320°K. The intensity is very weak, and it is not explained in our work. At about 0°C, all the paramagnetic hole centers are completely annealed. This is checked by cooling the sample to 80°K and looking by means of EPR for the hole spectrum.

Our high-resolution thermoluminescence spectra of Gd^{3+} in SrF_2 and BaF_2 show that both cubic and axial symmetry rare-earth ions are converted to the divalent state. In CaF₂ it has been shown that after irradiation only cubic-symmetry divalent ions are found.^{6,19,20} In BaF₂, however, Tm²⁺ is found in trigonal and cubic symmetry, and the possibility of switching from one symmetry to another by light illumination has been demonstrated.²¹ At lowest temperatures, the recombination of hole and Re²⁺ occurs in the axial symmetry

¹⁹ W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) 81, 371 (1963).
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²¹ E. S. Sabisky and C. H. Anderson, Phys. Rev. 159, 234 (1967).

site. The pair Re²⁺-F⁻ attracts a hole. In higher temperatures, the cubic converted sites recombine.

A more detailed study of the V_{K} is needed in order to establish the trapping mechanism by a local negative charge more precisely. Electron-nuclear double-resonance measurements probably are needed. The details of the self-trapping process could be revealed also by this technique.

The complexity of the centers in CaF_2 does not allow us to understand the nature of the six glow peaks² found there.

In conclusion, we would like to point out that we found two new centers in SrF_2 and BaF_2 , namely, V_H and V_{K}' centers. The nature of the V_{H} centers is well established in this work. An experimentally verified model is given to explain the existence of various thermoluminescent glow peaks.

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Optical Phonons and Symmetry of Tysonite Lanthanide Fluorides

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The polarized infrared reflectance of LaF₃, CeF₃, PrF₃, and NdF₃ has been measured from 40 to 500 cm⁻¹ at 295, 78, and 7°K. Kramers-Kronig analyses of the reflectance spectra yield evidence for eleven infraredactive phonons in the σ polarization ($E \perp c$) and six in the π polarization ($E \parallel c$). These results, together with reported magnetic-resonance measurements, are consistent with a $P\bar{3}'c'1$ magnetic space group. A theory and method for directly observing the longitudinal optical phonon frequencies of strongly anisotropic crystals in transmission are reported.

INTRODUCTION

HE partially filled 4f electron shell of the lanthanide elements is so well screened from its external environment that, when the ions are held in a suitable host lattice, electronic transitions of the type $4f \rightarrow 4f$ are expected to give sharp spectral lines. Some of the known $4f \rightarrow 4f$ transitions lie in the far-infrared region of the spectrum.¹⁻⁵ Consequently, there is currently strong motivation to assess the potential of these lowenergy transitions for use in solid-state far-infrared lasers.

It is clear, however, that in order to investigate these potential far-infrared lasing systems, the host lattice must be chosen with care. This is true not only because the host lattice will determine the position and linewidth of the $4f \rightarrow 4f$ transitions, but also because the optically active phonon frequencies of most solids lie within the far-infrared region as well, and precautions should be taken to ensure that the frequencies of the electronic and phonon excitations do not significantly overlap.

The tysonite structure of LaF₃, CeF₃, PrF₃, and NdF₃ provides a convenient host lattice in which other lanthanide ions will enter substitutionally. These substances are rugged^{6,7} and readily available in singlecrystal form.⁸ Their nonhygroscopic nature^{6,7} has the spectroscopic advantage that they are unlikely to incorporate OH- impurities which are well known to

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Grant No. GP-4923. ‡ Work supported in part by the Joint Services Electronics Program [Contract No. DA 28-043-AMC 02536 (E)], by NASA [Grant No. NGR 22-009-(237)], and by the U. S. Air Force [ESD Contract No. AF 19(628)-6066]. ¹ S. A. Johnson, H. G. Freie, A. L. Schawlow, and W. M. Yen, J. Opt. Soc. Am. 57, 734 (1967). ² R. A. Buchanan, H. E. Rast, and H. H. Caspers, J. Chem. Phys. 44, 4063 (1966). ³ W F. Krunka and J. P. Cruther, J. Chem. Phys. 20, 1024

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