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Infrared and electron-paramagnetic-resonance spectra of trivalent rare-earth ions in hydrogenated strontium-fluoride crystals*

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Infrared measurements of hydrogenated strontium-fluoride crystals containing trivalent rare-earth ions, and EPR measurements of hydrogenated strontium-fluoride crystals containing gadolinium are reported. The infrared results show that the hydride ions associated with the rare-earth ions occur in several different sites whose relative occurrence changes abruptly in the vicinity of holmium. For the rare-earth ions before holmium in the rare-earth series, there are two principal sites. One of these has tetragonal symmetry and the other rhombic symmetry. These two sites, and two additional sites of rhombic symmetry, are also observed in the case of the gadolinium-doped crystal by EPR. For the heavier rare-earth ions beyond holmium in the rare-earth series, the tetragonal and rhombic symmetry sites are replaced by a low-symmetry site. Additional sites produced by ultraviolet irradiation of the crystals and the sites observed in the hydrogenated barium-fluoride crystals containing trivalent rare-earth ions are also described. Possible models for the various sites are proposed.

I. INTRODUCTION

Trivalent rare-earth ions introduced as impurities into alkaline-earth fluoride crystals require charge compensation, and it is now well established that interstitial fluoride ions are the major compensating mechanism. However, in hydrogenated crystals, hydride ions may also be involved in charge compensation. In this case the various charge-compensation arrangements can be studied by examining the infrared spectra of the localized modes of the hydride ions. The number and magnitude of the frequencies observed for a particular hydride-ion site allow determination of its symmetry and the vibrational force constants. The relative occurrence of different sites is found to depend on the particular rare-earth ion present, on its concentration, and on the thermal history of the crystal during and after hydrogenation. Additional sites, including those unstable at room temperature, can be produced by ultraviolet irradiation at low temperatures. Investigations of this type have already been reported for rare-earth ions in calcium fluoride.[1]

Electron paramagnetic resonance (EPR) can also be used to determine site symmetries and charge-compensation arrangement for rare-earth ions. Numerous EPR investigations have been carried out on rare-earth ions in calcium-fluoride crystals both before and after hydrogenation.[2]

In this paper we give a description and analysis of the hydride ion in several positions in the strontium-fluoride lattice. Infrared measurements of hydrogenated strontium-fluoride crystals containing almost all the rare-earth ions as well as yttrium are described in Sec. IV, while EPR measurements on the crystals containing gadolinium are given in Sec. III. Infrared results for hydrogenated barium-fluoride crystals containing rare-earth ions are also included in Sec. IV.

II. EXPERIMENTAL TECHNIQUES

The strontium- and barium-fluoride crystals containing rare-earth ions used in these investigations were grown by the Stockbarger method using optical-grade strontium and barium fluorides purchased from Optovac Inc., and the rare-earth fluorides or oxides. Oxygen was removed from the melt by using lead fluoride as a scavenger. The crystals were grown in an A. D. Little Inc. 38-kW radio-frequency furnace using a helium atmosphere. Rare-earth-ion concentrations of 0.05 and 0.3 at.% were used for most crystals. The 0.05-at.% concentration gave adequate intensity of absorption lines yet was low enough to ensure that only inappreciable quantities of complex rare-earth–hydride-ion clusters were formed.[1]

Hydrogen or deuterium was introduced into the crystals by the method of Hall and Schumacher,[3] which involves heating the samples at around 800 °C in contact with aluminium and in a hydrogen or deuterium atmosphere. In order to enhance the concentration of simpler hydride ion sites, the crystals were quenched to 77 °K directly after the treatment by immersing the quartz hydrogenation tube in liquid nitrogen. The concentration of hydrogenic tetragonal symmetry ion sites obtained was typically $\frac{1}{20}$ of the corresponding fluoride-ion site.

Infrared measurements were made on a Beckman IR12 spectrophotometer. This instrument has a maximum resolution of 0.3 cm^{-1} in the region of 1000 cm^{-1}, where most of the measurements were taken. It was calibrated using the accurately known infrared lines of water vapor, carbon dioxide, and ammonia, and accuracy was maintained to ±0.6 cm^{-1}. A conduction-type Dewar with cesium-iodide windows was used for low-temperature work. The crystals were clamped to a copper block in contact with the helium reservoir, using indium foil to maximize the heat transfer.

EPR measurements were made using a Q-band (35 GHz) spectrometer. This was favored over those operating at X band (9 GHz) for the work on trivalent gadolinium ions because of the large zero-field splittings observed for the sites reported here. The spectrometer is of conventional homodyne design. Two magnetic field modulations were employed: 50 Hz for visual presentation of the EPR signal on an oscilloscope which aids sample alignment adjustments, and 660 Hz for chart recording of the spectra using a tuned phase-sensitive detection system. The sensitivity was estimated as 10^{15} spins. Magnetic fields were measured to ±2 G using an N.M.R. probe, while the microwave frequency was determined using DPPH (α, α'-diphenyl-β-picryl hydrazyl) as a g marker. TE_{001}-mode cylindrical cavities were used with side coupling to various waveguide feed arrangements, and their axes could be either vertical or horizontal. The crystals were usually mounted with the [110] axis parallel to the sample holder axis. This was achieved on an optical goniometer by using reflections from the (111) cleavage planes, which intersect along a [110]-type direction. With the sample holder axis in a vertical direction the (110) plane, which contains the three axes [001], [111], and $[1\bar{1}0]$, could be conveniently studied. The (001) plane is accessible with the sample axis horizontal.

Ultraviolet irradiations were performed on the crystals mounted in a cavity, equipped with quartz windows, immersed directly in liquid nitrogen. The subsequent EPR measurements were made by overpressurizing the waveguide and cavity with nitrogen gas to expel liquid nitrogen from the cavity. This method of irradiation eliminated sample heating due to the 500-W mercury lamp used, and consequent site-instability problems.

The spin Hamiltonian parameters were mainly determined by a least-squares-fitting program, but in those cases where only a few line positions were measured, first-order perturbation theory was used.

III. EPR SPECTRA OF HYDROGENATED STRONTIUM-FLUORIDE CRYSTALS CONTAINING GADOLINIUM

Crystals of strontium fluoride containing 0.05-at.% gadolinium trifluoride which have been hydrogenated show EPR spectra characteristic of the tetragonal C_{4v} site and the trigonal C_{3v} site observed in the parent crystals.[4] In addition, many new sets of lines appear with intensities much less than the parent crystal lines. The weak intensity and low symmetry of the various hydrogenic sites result in complex spectra of overlapping lines as shown in Fig. 1. Consequently only those lines remote from the central $g = 2$ region could be un-

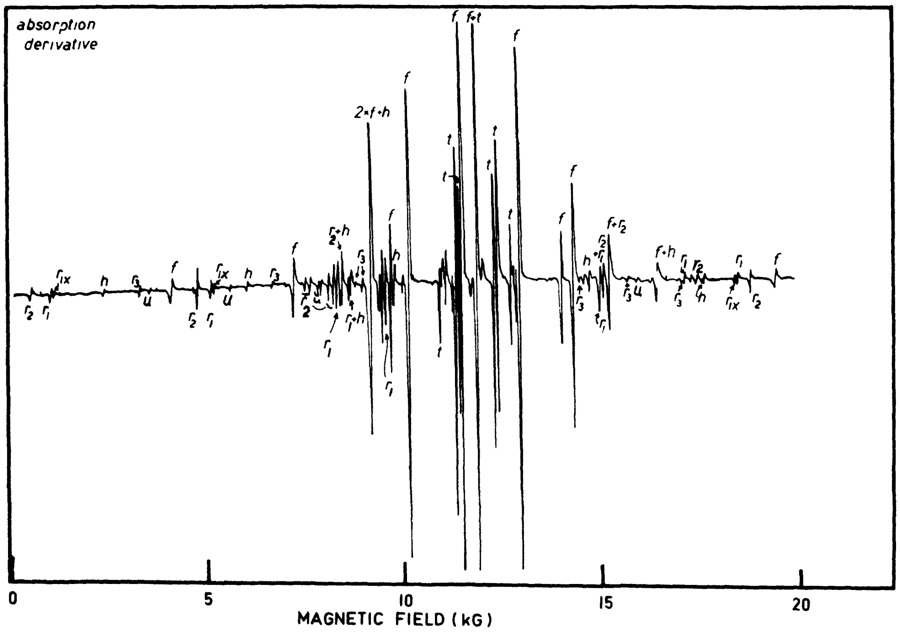

FIG. 1. Q-band (34.5 GHz) EPR spectrum of hydrogenated strontium fluoride doped with 0.05-at.% gadolinium trifluoride for the magnetic field parallel to the [001] axis. The lines of the tetragonal and trigonal symmetry fluoride ion sites are labeled f and t, respectively. Lines of the three rhombic and one tetragonal symmetry hydrogenic sites are labeled r_1, r_2, r_3, and h, respectively.

ambiguously identified. By examining the EPR spectra of some 20 crystals it was found that there are four main hydrogenic sites, whose relative intensities depend on the temperature of hydrogenation and the subsequent thermal treatment of the crystals. Several sets of weaker lines were also observed but these were too difficult to examine in any detail. They are discussed in Sec. III C.

The four main sites consist of three rhombic sites, henceforth labeled R_1, R_2, and R_3, and one tetragonal site. Crystals which were hydrogenated at temperatures in excess of 900 °C contained all four sites in similar concentrations. However, when samples were hydrogenated at 800 °C and subsequently quenched in liquid nitrogen, only the tetragonal and R_3 sites were observed. After such a crystal was left at room temperature for 24 h, the R_1 site appeared and grew exponentially to its maximum intensity in a few weeks. Crystals which had been stored for a few weeks at room temperature showed an R_2 spectrum which grew more intense in subsequent months. After a period of six months the EPR spectra of these crystals were indistinguishable from those hydrogenated at high temperatures.

A. Tetragonal symmetry site

In this site, the hydride ions are located at the center of the empty fluorine cube adjacent to the trivalent rare-earth ion. This site, henceforth referred to as the hydrogenic C_{4v} site, was readily identified by the simple angular variation of its spectrum around the [001] direction. Sufficient absorption lines were observed for this site from the $\vec{H} \parallel \vec{z}$ and $\vec{H} \parallel \vec{x}$ field orientations to enable all the parameters in the spin Hamiltonian to be evaluated. The EPR lines shift slightly when either deuterium or tritium is subsituted for the hydrogen and the spin Hamiltonian parameters for all three isotopes of hydrogen are listed in Table I. The isotope shifts are larger than observed for calcium fluoride while the axial field parameters are smaller.[5] A factor of 0.76 relates the parameters of the hydrogenic C_{4v} site in strontium fluoride to those in calcium fluoride. This is the same ratio as found for the corresponding fluoride ion sites in the two crystals.

B. Rhombic R_1 and R_3 sites

These two sites bear a strong resemblance to the site produced by liquid-nitrogen-temperature irradiation of calcium-fluoride crystals containing gadolinium. The spectra of all three sites are, therefore, considered together. The irradiation induced site in calcium fluoride is also labeled

TABLE I. Spin-Hamiltonian parameters of hydrogenic, deuterium, and tritium C_{4v} sites in calcium and strontium fluorides containing gadolinium. The units are in cm^{-1} and the parentheses enclose the uncertainty expressed in units of the last significant digit.

Site	Temp. (°K)	Host crystal	$g_\parallel$	$g_\perp$	b_2^0	b_4^0	b_6^0	b_4^4	b_6^4	No. of lines measured	Standard deviation (G)	Standard deviation (cm^{-1})
H	295	CaF_2	1.9921(5)	1.9920(5)	−0.184 14(5)	−0.002 39(5)	−0.000 09(3)	−0.011 48(15)	+0.000 75(30)	12	0.4	0.4×10^{-4}
	77		1.9938(10)	1.9911(10)	−0.192 32(10)	−0.002 54(10)	−0.000 05(6)	−0.011 38(30)	+0.000 88(60)	8	1.3	1.2×10^{-4}
D	295	CaF_2	1.9923(5)	1.9924(5)	−0.186 00(5)	−0.002 32(5)	−0.000 08(3)	−0.011 36(15)	+0.000 53(30)	12	1.6	1.5×10^{-4}
	77		1.9938(10)	1.9914(10)	−0.194 65(10)	−0.002 52(10)	−0.000 05(6)	−0.011 30(30)	+0.000 64(60)	8	3.0	2.7×10^{-4}
T	295	CaF_2	1.9916(8)	1.9924(8)	−0.186 83(8)	−0.002 36(8)	−0.000 07(5)	−0.011 31(20)	+0.000 34(45)	10	4.1	3.7×10^{-4}
H	295	SrF_2	1.9916(6)	1.9916(6)	−0.139 85(6)	−0.002 04(6)	−0.000 06(3)	−0.011 34(20)	+0.000 62(40)	18	2.7	2.5×10^{-4}
D	295	SrF_2	1.9923(6)	1.9923(6)	−0.142 11(6)	−0.002 03(6)	−0.000 05(3)	−0.011 03(20)	+0.000 84(40)	18	2.9	2.7×10^{-4}
T	295	SrF_2	1.9927(6)	1.9921(6)	−0.143 23(6)	−0.002 01(6)	−0.000 05(3)	−0.011 47(20)	−0.000 08(40)	10	2.4	2.2×10^{-4}

R_3 because of its exact analogy to the R_3 site reported here for strontium fluoride. However, it is only observed at 77 °K, while both strontium-fluoride sites are stable at room temperature and ultraviolet irradiation at 77 °K does not appreciably increase the intensity of their EPR lines. The $\vec{H}\parallel[001]$ spectra of all three sites consist of seven degenerate quadruplets and seven degenerate octets. When the field is rotated away from the [001] direction in the (110) plane, the quartets split into two singlets and a doublet. A least-squares fitting revealed that the overall splittings reached a maximum at tilt angles of 3.2°, 2.5°, and 3° (all ± 0.5°) from the [001] axis for the R_3 site of calcium fluoride and the R_1 and R_3 sites of strontium fluoride, respectively. When the field is rotated away from the [001] axis in the (100) plane, each quartet splits into two doublets.

The R_3 site for calcium fluoride was also examined along the [111] direction. This was not possible for either of the strontium-fluoride sites because of the difficulty of distinguishing their EPR lines from the multitude of other lines due to other sites. In place of the degenerate triplets obtained for a tetragonal symmetry site in this direction there are groups of lines, consisting of two triplets and a hextet.

All features of the R_3 site in calcium fluoride are consistent with 12 magnetically inequivalent sites of rhombic (C_s) symmetry with the only symmetry element for each magnetically inequivalent site being a reflection in a (110) type plane. If the x-z plane is chosen as the plane of reflection symmetry the spin Hamiltonian involves only real parameters:

$$\mathcal{H} = \mu_B(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + \sum_{n=1}^{3} \sum_{m=0}^{2n} B_{2n}^{m} O_{2n}^{m}. \tag{1}$$

To a very good approximation, the g value may be assumed isotropic and, in this case, the x axis may be chosen to lie anywhere in the $(\bar{1}10)$ plane. The axis system chosen is x along [110], y along $[\bar{1}10]$, and z along [001]. The spin Hamiltonian has 18 parameters and the experimental data is inadequate to determine all these. The spin Hamiltonian may therefore be approximated by one with a dominant tetragonal symmetry along the [001] axis, with a weaker rhombic perturbation represented by $n = 2$ terms only:

$$\mathcal{H} = g\vec{H}\cdot\vec{S} + (B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_4^4) + B_2^1 O_2^1 + B_2^2 O_2^2. \tag{2}$$

The EPR spectrum of the calcium-fluoride R_3 site for $\vec{H}\parallel[111]$ shows a definite and well-resolved isotope shift between hydrogenated and deuterated crystals, while no shift was observed for $\vec{H}\parallel[001]$. The spin-Hamiltonian parameters which give the best least-squares fit of the $\vec{H}\parallel[001]$, $\vec{H}\parallel[010]$, and $\vec{H}\parallel[111]$ spectra of both the hydrogenic and the deuterium R_3 sites for calcium fluoride are given in Table II.

The truncated spin Hamiltonian (2) was again used for the R_1 and R_3 sites in strontium fluoride and the evaluated parameters are also given in Table II. The R_3 site for strontium fluoride also does not display an isotope shift for $\vec{H}\parallel[001]$. Furthermore it exactly resembles the calcium fluoride R_3 site in having the same ratio of b_2^0 parameters as the hydrogenic C_{4v} sites for the two crystals and an almost identical tilt angle. It is therefore plausible to ascribe the same charge-compensating arrangement to the two R_3 sites. Models for this site were developed from the data as follows.

An intersitital fluoride ion at the 001 position is almost certainly involved. The near tetragonal symmetry of the site indicates the presence of a charge-compensating anion at this position while the similarity of the b_2^0 values for the R_3 sites and the fluoride ion C_{4v} sites together with the zero isotope shift for $\vec{H}\parallel[001]$ shows that this anion is a fluoride rather than a hydride ion. Since the R_3 site does show an isotope shift for $\vec{H}\parallel[111]$, a hydride ion must also be involved and this must lie somewhere in the $(\bar{1}10)$ plane to satisfy the spectral symmetry. For overall charge neutrality, the hydride ion would not be in an interstitial site, but would occupy a substitutional site. Two possible models consistent with the above are shown in Fig. 2. The first is favored because it can be derived more simply from the hydrogenic C_{4v} site by an interstitialcy type motion. Taking the case of calcium fluoride containing gadolinium under irradiation, one of the four fluoride ions, which are mutual neighbors of the trivalent gadolinium and hydride ions, is displaced to one of the two adjacent unoccupied interstitial sites. The hydride ion then moves into the vacancy left by the displaced fluoride ion. The formation of the alternative model from the hydrogenic C_{4v} site requires an additional jump of the fluoride ion to the 001 position (Fig. 3).

The model for the R_1 site is less certain. This site shows an isotope shift for $\vec{H}\parallel[001]$ comparable to that found for the hydrogenic C_{4v} site and hence an interstitial hydride ion is expected in the 001 position. Using the same reasoning as for the R_3 site, a possible model is that given in Fig. 4. This can be formed from the hydrogenic C_{4v} site by the substitution of a migratory hydride ion, for one of the regular fluoride ions.

TABLE II. Spin-Hamiltonian parameters for rhombic gadolinium sites in hydrogenated and deuterated calcium and strontium-fluoride crystals. These parameters are related to the parameters of Eq. (2) by $b_2^m = 3B_2^m$, $b_4^m = 60B_4^m$, and $b_6^m = 1260B_6^m$. Units are in cm^{-1} and the parentheses enclose the uncertainties expressed in units of the last digit.[a]

Host crystal	Site	Temp. (°K)	g	b_2^0	b_4^0	b_6^0	b_4^4	b_6^4	b_2^1	b_2^2	Standard deviation (cm^{-1})	Standard deviation (G)	Number of lines
CaF_2	$R_3(H^-)$	77	1.990(2)	0.1665(2)	0.0022(2)	0.000 02(10)	−0.0147(5)	0.0008(5)	0.030(10)	0.0011(10)	0.0019	16.7	29
CaF_2	$R_3(D^-)$	77	1.990(2)	0.1665(2)	0.0022(2)	0.000 02(10)	−0.0147(5)	0.0008(5)	0.029(10)	0.0023(10)	0.0020	17.0	29
SrF_2	$R_1(H^-)$	295	1.993(2)	0.1612(2)	0.0019(2)	0.000 09(10)	−0.0094(7)	0.0009(5)	...	0.015(10)	3.5×10^{-4}	3.7	11
SrF_2	$R_1(D^-)$	295	1.991(2)	0.1637(2)	0.0021(2)	0.000 06(10)	−0.0108(7)	0.0012(5)	...	0.031(10)	3.7×10^{-4}	3.9	11
SrF_2	$R_2(H^-)$	295	1.992(2)	0.1693(2)	0.0021(2)	0.000 1(2)	...	...	...	...	...	...	...
SrF_2	$R_2(D^-)$	295	1.993(2)	0.1710(2)	0.0021(2)	0.000 0(2)	...	...	...	...	...	...	...
SrF_2	$R_3(H^-, D^-)$	295	1.993(2)	0.1250(2)	0.0019(2)	0.000 1(2)	−0.0128(5)	+0.0002(2)	...	...	4.3×10^{-4}	4.5	8
SrF2	$R_{2x}(H^-)$	295	1.993(2)	0.1706(2)	0.0020(2)	0.000 0(2)	...	...	...	...	...	...	...
SrF_2	$R_{2x}(D^-)$	295	1.993(2)	0.1726(2)	0.0022(2)	0.000 1(2)	...	...	...	...	...	...	...
SrF_2	$R_{1x}(H^-)$	295	1.991(2)	0.1594(2)	0.0022(2)	0.000 2(2)	...	...	...	...	...	...	...
SrF_2	$R_{1x}(D^-)$	295	1.992(2)	0.1601(2)	0.0022(2)	0.000 1(2)	...	...	...	...	...	...	...

[a] Parameters for those sites for which standard deviation are not listed were determined by first-order perturbation theory.

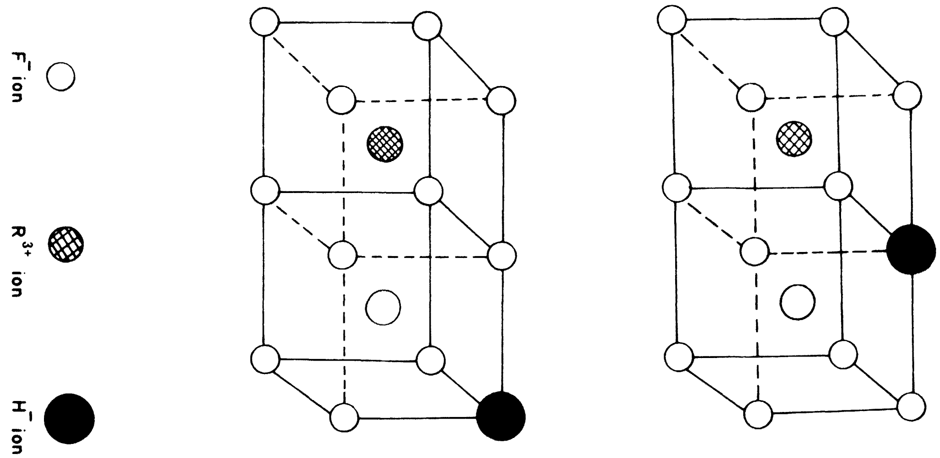

FIG. 2. Proposed models for the rhombic symmetry R_3 site.

C. R_2 site

The experimental observations on the R_2 site are more difficult to analyze than those of the R_1 and R_3 sites. The EPR spectra of the latter sites consist of a set of seven degenerate quadruplets. This pattern is almost reproduced for the R_2 site except that the outermost lines $(\pm\frac{7}{2}\rightarrow\pm\frac{5}{2})$ lines for $\vec{H}\parallel[001]$ are resolved into two fourfold-degenerate lines separated by 24 G at 35.6 GHz. An isotope shift and tilt angle similar to that of the R_1 site are observed. The extra structure on the outermost line cannot be classed as superhyperfine as it is the same for both the hydrogenated and deuterated crystals. The R_2 site is a small perturbation of a C_{4v} site and the isotope shift indicates that the C_{4v} site must be a hydrogenic one.

In some crystals, satellite lines were observed close to the EPR lines of the R_1 and R_2 sites. These are caused by perturbations of these sites by adjacent lattice defects. The approximate spin-

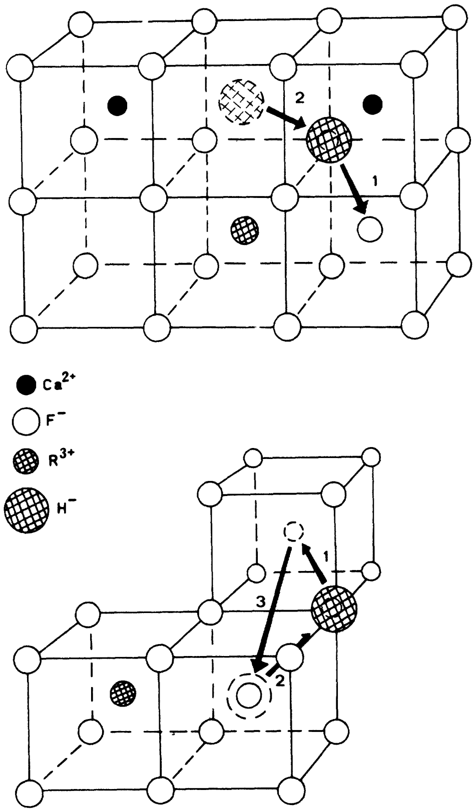

FIG. 3. Two models for the rhombic symmetry R_3 site showing how these can be derived from the hydrogenic C_{4v} site by interstitial motion. The dotted spheres show the original or transitory position of the ions. In both cases, the interstitial hydride ion of the hydrogenic C_{4v} site dislodges a lattice fluoride ion to an interstitial site (arrow marked 1), and takes its place (arrow 2). In the second model, a further jump (arrow 3) of the fluoride ion to the 001 position is required.

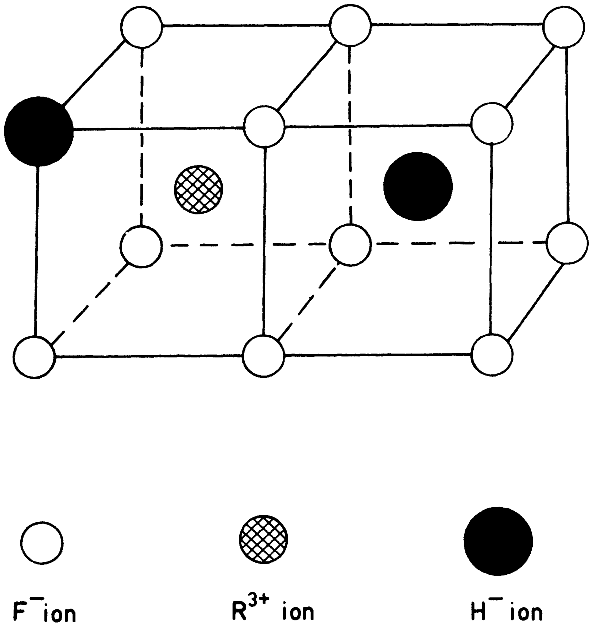

FIG. 4. Proposed model for the rhombic symmetry R_1 site.

Hamiltonian parameters of these perturbed sites (denoted R_{1X} and R_{2X}) are listed in Table II.

IV. INFRARED SPECTRA

The crystals were examined in the infrared from 700 to 1300 cm^{-1}. Typical spectra recorded at 77°K for the 0.05% crystals are shown in Fig. 5. The 0.3% spectra are more complex than the 0.05% spectra, but show the same overall trends with change of the rare-earth ion.

Several of the local mode lines have frequencies independent of the particular rare earth present and are also observed in hydrogenated crystals of undoped strontium fluoride. Of these, the strong line at 892.8 cm^{-1} is the well established tetrahedral site line due to hydride ions replacing fluoride ions in the substitutional positions of the lattice.[6] Other lines arise from perturbations of this line and form satellites about it.

The major remaining lines have frequencies that vary with the rare-earth ion present. By studying the spectra of many crystals, it is found that these lines may be assigned to three main hydride ion sites which are associated with the rare-earth ions. Two of these three sites are observed only for the lighter rare-earth ions and are characterized for the case of gadolinium by EPR measurements. These are the hydrogenic C_{4v} site and the rhombic R_1 site, both of which are described in Sec. III.

These two sites are superseded for the heavier rare-earth ions beyond terbium by a third site of low symmetry. The data for this site is insufficient to uniquely determine the position of the hydride ion relative to the rare-earth ions, and several possible models are proposed.

A. Hydrogenic C_{4v} site

The two most prominent infrared local mode lines are analogs of the corresponding lines of the hydrogenic C_{4v} site observed in hydrogenated calcium-fluoride crystals containing low concentrations (0.05 at.%) of rare-earth ions.[1] This assignment is confirmed by EPR measurements carried out on hydrogenated strontium-fluoride crystals containing cerium,[7] neodymium,[7] and gadolini-

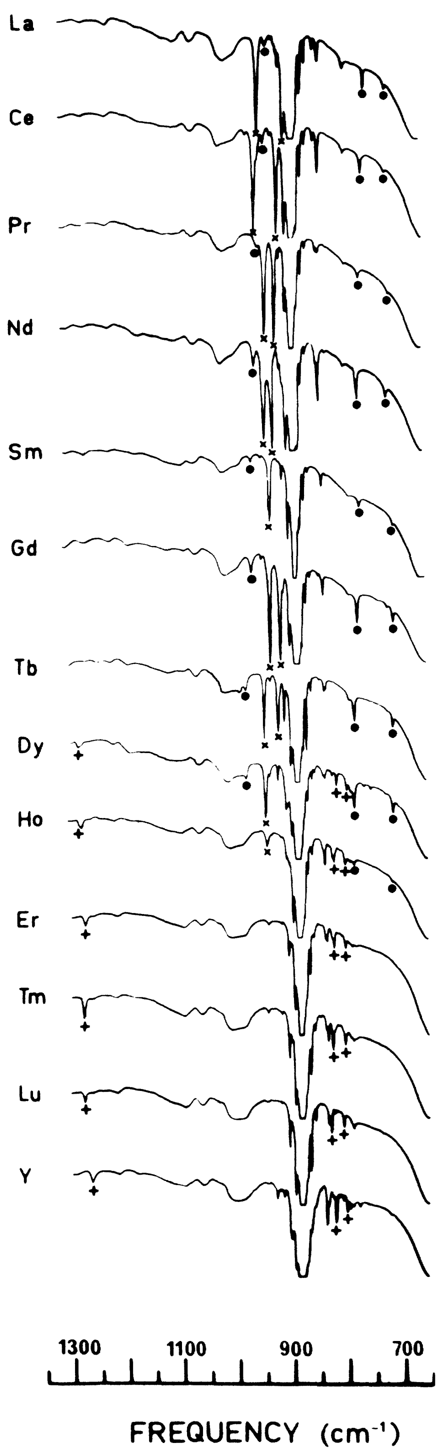

FIG. 5. 77 °K infrared absorption spectra of hydrogenated strontium-fluoride crystals containing 0.05 at% of trivalent rare-earth fluorides. The symbols ×, ●, and + denote the hydrogenic C_{4v} site, the rhombic C_s site, and the low-symmetry site, respectively.

um (Sec. III A). In all cases a good correlation was obtained between the EPR spectra for the hydrogenic C_{4v} site and the infrared lines observed here.

The frequencies, linewidths, and relative intensities of the infrared absorption lines for this site, observed in the 0.05-at.% concentration crystals are given in Table III. The lines for the case of europium were produced by x irradiation of the crystals after their hydrogenation, as was done by Chambers and Newman[8] for calcium-fluoride crystals containing europium.

A plot of the frequencies at 77°K against ionic radii of the various rare-earth ions is given in Fig. 6. The separation of the two lines initially decreases along the rare-earth series, and the lines become almost coincident at samarium. Beyond samarium, they separate again until terbium is reached. For the two rare-earth ions following terbium, i.e., dysprosium and holmium, one of the lines of the site is no longer observable as it is swamped by the intense absorption of the tetrahedral site line at 892.8 cm^{-1} and its satellites. Beyond holmium, the site becomes unfavorable and neither of the lines can be observed.

Examination of the linewidths and relative intensity of the two hydrogenic lines shows that they vary systematically along the rare-earth series and cross over in the vicinity of samarium.

For the rare-earth ions before samarium, the lower-frequency line is narrower and has a slightly smaller intensity (Table III) and is the double degenerate (x, y) transverse vibrational mode. The higher-frequency line is the longitudinal (z) vibrational mode.

The assignment is based on the electron phonon interaction splitting of the lower-frequency line observed by Jacobs *et al.*[9] in the hydrogenated strontium-fluoride crystals containing cerium.

After samarium, the lower-frequency line becomes the wider and more intense line of the two, and is assigned as the longitudinal (z) vibration while the higher-frequency line is the double degenerate transverse (x, y) vibration. A high-resolution scan at 15°K of the single line observed in the case of samarium shows that the lines have not yet crossed over and the assignment is as for the cerium lines.

Although yttrium is not a rare-earth ion, strontium-fluoride crystals containing yttrium have analogous lines at 924.4 ± 1.0 and 936.7 ± 0.9 cm^{-1}. The lines of yttrium usually fit into the sequence of ionic radii between holmium and erbium [Sec. IV D and Ref. 1] so if these lines are assigned to the hydrogenic C_{4v} site this supports the presence of this site in both the dysprosium and holmium crystals.

TABLE III. Frequencies, linewidths, and intensities of the hydrogenic C_{4v} site in hydrogenated strontium-fluoride crystals containing 0.05 at.% of rare-earth ions recorded at 77 °K.

Rare-earth ion	(x, y) frequency (cm^{-1})	Linewidth (cm^{-1})	(z) frequency (cm^{-1})	Linewidth (cm^{-1})	Intensity relative to the (x, y) line
La	905.5 ± 0.7 [a]	1.5 ± 0.3	950.7 ± 0.8	2.6 ± 0.3	1.1
Ce	917.5 ± 0.7 [a]	2.3 ± 0.3	956.6 ± 0.8	3.0 ± 0.3	1.2
Pr	921.1 ± 0.8	2.2 ± 0.3	938.9 ± 0.8	3.4 ± 0.3	1.2
Nd	927.0 ± 0.7	1.9 ± 0.3	941.5 ± 0.8	3.4 ± 0.3	1.2
Sm	934.1 ± 0.8 [b]	...	936.5 ± 0.8 [b]	...	...
Sm (15 °K)	934.1 ± 0.7	1.0 ± 0.3	937.0 ± 0.7	1.0 ± 0.3	1.1
Eu	934.5 ± 0.7	2.0 ± 0.3	919.2 ± 0.8	3.1 ± 0.4	1.7
Gd	937.4 ± 0.8	1.7 ± 0.3	919.3 ± 0.7	2.6 ± 0.3	1.2
Tb	948.8 ± 0.7	3.0 ± 0.3	924.4 ± 0.7	3.8 ± 0.3	1.0
Dy	948.8 ± 0.8	4.4 ± 0.3	...	...	...
Ho	947.0 ± 1.0	6.2 ± 1.0	...	...	...

[a] Partially obscured by the strong absorption due to the tetrahedral site line at 892.8 cm^{-1}.

[b] Not completely resolved at 77 °K.

B. Interaction between the adjacent rare-earth and hydride ions

The hydride ion in the C_{4v} symmetry site moves in a potential well which may be expanded as a power series in the hydride-ion displacements:

$$V = a(X^2 + Y^2) + bZ^2 + cZ^3 + dZ(X^2 + Y^2) + f(X^4 + Y^4) + gZ^4 + hZ^2(X^2 + Y^2) + kX^2Y^2. \tag{3}$$

The hydride ion interacts with this potential both through its point charge q and its dipole moment p. The harmonic constants a and b evaluated on an ionic model have the form[9]

$$a = A + \tfrac{1}{2}\sigma q/D^3 + p\sigma/D^4 - 2Ap/qD, \tag{4}$$

$$b = A - \sigma q/D^3 - 3p\sigma/D^4. \tag{5}$$

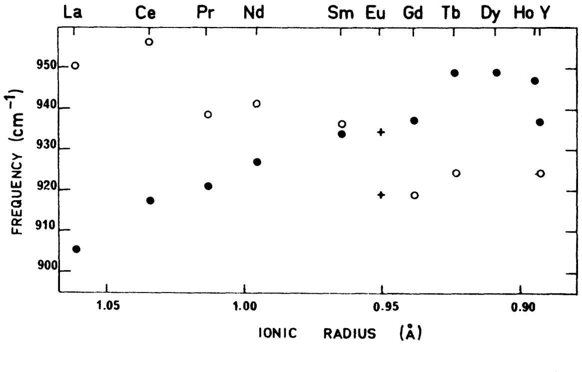

FIG. 6. Frequencies of the hydrogenic C_{4v} site local mode lines in hydrogenated strontium-fluoride crystals containing 0.05-at.% rare-earth ions as a function of the trivalent rare-earth ion radius. The (x, y) and z local mode lines are identified by the symbols ● and ○ respectively. The europium lines, produced by irradiation, are marked +.

Here D is the distance between the rare-earth ion and the equilibrium position of the hydride ion, σ is the effective charge on the rare-earth ion, and A is the constant of the harmonic potential for an isolated hydride ion in the interstitial site. The observed frequencies of the hydride ion in the cubic interstitial site and in the C_{4v} site are approximately the harmonic values

$$w_c = (2A/m)^{1/2}, \quad w_{x,y} = (2a/m)^{1/2}, \quad w_z = (2b/m)^{1/2}, \tag{6}$$

where m is the hydride ion mass. Jacobs *et al.*[9] took the local mode data for the gadolinium-doped crystals to be representative for the calculations of p for the case of calcium fluoride and obtained $P/e = 1.1$ Bohr radius for $q = \sigma = 0.85e$. For strontium fluoride, lanthanum was chosen as the ion for which the lattice is regarded as being substantially undistorted since Sr^{2+} and La^{3+} have similar ionic radii.[10] Cubic interstitial sites have not been observed in strontium fluoride and a value of 1212 cm^{-1} was deduced using as a scaling factor the ratio of the frequencies of the tetrahedral sites in strontium and calcium fluorides. With this, $P/e = 1.6$ Bohr radius was obtained for strontium fluoride, together with $q = \sigma = 0.98e$. The values obtained for other rare-earth ions are very similar because the decrease in the ionic separation D along the rare-earth series accounts almost wholly for the change in frequencies of the local mode lines. Within the approximations of the model, the observed frequencies indicate that there is less sharing of the trivalent rare-earth and hydride-ion charges and a greater hydride ion dipole moment for the larger strontium-fluoride lattice. The value of P/e is physically reasonable because P/e for a free hydride ion has been measured for small fields to be 7.7 Bohr radius,[11] and this is expected to be considerably smaller for a hydride ion in a solid.

C. Rhombic C_s site

Three localized mode lines due to hydrogen are assigned to a rhombic site of C_s symmetry. Two of these lines lie on the low-frequency side of the tetrahedral site line and the third on the high-frequency side (Fig. 5 and Table IV). The relative intensities of the three lines in the same and different rare-earth-doped crystals agree within the uncertainities of the intensity measurements. In order of increasing line frequency, they are in the ratio 0.4 ± 0.2, 1.0 ± 0.4, and 0.9 ± 0.4. As for the hydrogenic C_{4v} site, the local mode lines of this site are not observed beyond holmium in the rare-earth series. Figure 7 gives a plot of the line frequencies at 77 °K against the rare-earth ionic radius.

The assignment of these three lines to a site having rhombic symmetry is based on their correlation with the EPR lines of the R_1 site described in Sec. III. The intensity of this rhombic site varies markedly with the temperature of the hydrogenation and is weaker at lower hydrogenation temperatures. After hydrogenation at 750 °C and quenching in liquid nitrogen, both the infrared and EPR lines due to this site could barely be detected. After several hours at room temperature, both sets of lines gained in intensity and showed a good correlation (Fig. 8).

The EPR analysis of Sec. III shows that the R_1 rhombic site is a modification of the hydrogenic C_{4v} site (Fig. 4). The infrared data are consistent with this model. Three infrared local mode lines would arise from the substitutional site hydride ion while the local mode lines of the interstitial site would be masked by the lines of the unperturbed hydrogenic C_{4v} site also present in the crystal. The infrared spectra could equally well be assigned to a model having a fluoride interstitial ion charge compensating the rare-earth ion.

To distinguish between the two possibilities, infrared measurements were made of the spectra of lanthanum-, cerium-, and gadolinium-doped crystals containing a mixture of hydrogen and deuterium. If the rhombic site does involve two hydride ions, additional lines due to a substitutional hydride—interstitial deuterium ion pair should appear adjacent to the observed lines. Such a slightly displaced line was found for the case of the highest-frequency local mode line only (Table IV). Cerium is anomalous in that its 940.8-cm^{-1} line also shifted to 943.5 ± 1.6 cm^{-1}. The other two local mode lines remain unchanged and gain no satellite lines. The presence of the

TABLE IV. Frequencies, linewidths, and intensities of the C_s site local mode lines in hydrogenated strontium-fluoride crystals containing 0.05 at.% of rare-earth ions recorded at 77 °K.

Rare earth	Frequency (cm^{-1})	Linewidth (cm^{-1})	Frequency (cm^{-1})	Linewidth (cm^{-1})	Intensity relative to the lowest-frequency line	Frequency (cm^{-1})	Linewidth (cm^{-1})	Intensity relative to the lowest-frequency line	Frequency of the additional line in the hydrogen-deuterium crystal
La	725.5 ± 0.7	2.7 ± 0.5	763.3 ± 0.7	2.2 ± 0.5	2.2 ± 0.9	934.5 ± 1.0	5.8 ± 0.7	2.2 ± 0.9	929.0 ± 1.6
Ce	726.5 ± 1.4	5.5 ± 0.7	768.5 ± 0.7	3.5 ± 0.5	2.6 ± 1.1	940.8 ± 0.8	5.0 ± 1.3	2.8 ± 1.2	947.0 ± 1.6
Pr	721.0 ± 0.7	5.3 ± 0.5	772.7 ± 0.8	4.2 ± 0.5	2.1 ± 0.9	951.5 ± 0.8 [a]	7.3 ± 2.0	2.0 ± 1.4	
Nd	724.2 ± 0.7	3.5 ± 0.5	775.2 ± 0.7	2.9 ± 0.5	2.1 ± 0.8	957.8 ± 1.0	7.0 ± 2.0	1.9 ± 0.7	
Sm	719.6 ± 0.9 [b]	...	777.3 ± 0.7 [b]	...	...	966.7 ± 1.2 [b]	...	...	
Gd	720.6 ± 0.7	2.9 ± 0.5	784.2 ± 0.7	3.4 ± 0.5	2.5 ± 1.0	968.8 ± 0.9	5.5 ± 1.5	1.7 ± 0.6	965.0 ± 1.6
Tb	722.4 ± 0.8	2.9 ± 0.5	789.9 ± 0.7	3.9 ± 0.6	3.2 ± 1.0	980.6 ± 1.0 [c]	...	...	
Dy	722.3 ± 0.9	3.2 ± 0.5	792.3 ± 0.7	4.7 ± 0.5	2.4 ± 1.0	982.7 ± 1.1 [c]	...	...	
Ho	725.5 ± 0.9 [b]	...	792.5 ± 0.9 [b]	...	...	982.6 ± 3.8 [b,d]	...	...	

[a] Partially obscured by the absorption line at 938.9 cm^{-1} of the C_{4v} site.
[b] Not intense enough for linewidth and intensity measurements.
[c] Partially obscured by the strong absorption due to a phonon sideband of the tetrahedral site line at 985 cm^{-1}.
[d] Frequency obtained from the 0.3 at.% Ho spectra.

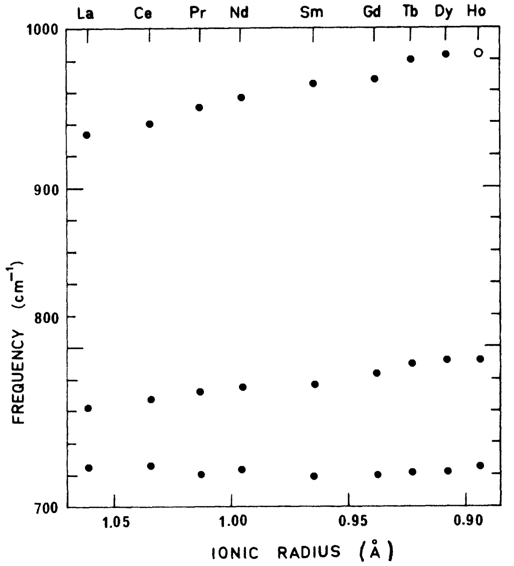

FIG. 7. Frequencies of the C_s site local mode lines in hydrogenated strontium-fluoride crystals containing 0.05-at.% rare-earth ions, as a function of the trivalent rare-earth ion radius. ○ frequency obtained from the 0.3-at.% Ho spectra.

additional line is taken as evidence for the C_s site having a hydride-ion charge compensator. This assignment is also supported by the fact that both the C_s site and the hydrogenic C_{4v} site are absent after holmium in the rare-earth series and the fluoride ion C_{4v} site is not expected to become unfavorable at exactly the same rare earth as the hydrogenic C_{4v} site.

With the model proposed in Fig. 4, the C_s site lines are assigned as follows: the neighboring trivalent rare-earth ion to the substitutional hydride ion in the C_s site gives a large splitting of the threefold-degenerate tetrahedral site line at 892.8 cm^{-1}. Two lines are then centered about the tetrahedral line one of which is doubly degenerate. The more distant interstitial charge compensating hydride ion splits the doubly degenerate line, and shifts the frequencies of all three lines. On this basis, the two lower-frequency lines are the two transverse (x, y) vibrations of the substitutional hydride ion in the C_s site and the highest-frequency line is the longitudinal (z) vibration. As the rare-earth ion radius decreases along the series, the substitutional hydride ion can move closer to the trivalent rare-earth ion resulting in larger separations of the local mode lines, as observed.

D. Low-symmetry site

The site appears only for rare-earth ions following terbium. The frequencies, line widths and relative intensities of the three local mode lines

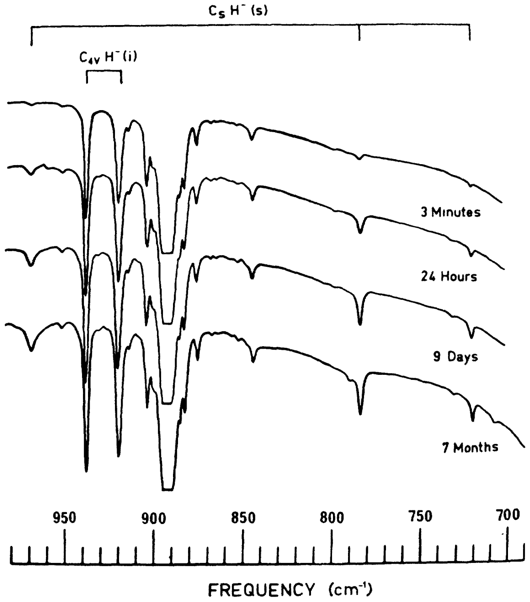

FIG. 8. 77 °K infrared spectra of hydrogenated strontium-fluoride crystals containing 0.05 at.% of gadolinium which have been hydrogenated at 750 °C and left at room temperature for the periods shown.

associated with this site are given in Table V. Two of the three lines lie on the low-frequency side of the tetrahedral site line and their frequencies increase along the series (Fig. 9). The third line lies on the high-frequency side of the tetrahedral site line and has an almost constant frequency except in the case of yttrium. The other yttrium lines fall between those of holium and erbium, in agreement with the ionic radii. No lines of this low-symmetry site were observed in the crystals containing ytterbium, even after x irradiation for 60 h.

The exact symmetry of this hydrogenic site is as yet unknown. There are a number of possible sites that the hydride ion could occupy to give the observed three line spectra. It is known from EPR measurements that the principal fluoride-ion charge-compensation arrangement in strontium-fluoride crystals changes along the rare-earth series from the fluoride ion C_{4v} site to a C_{3v} symmetry site arrangement in which the fluoride ion is located in the nearest interstitial position in the [111] direction.[12] This changeover in sites occurs between gadolinium and erbium and is therefore about the same rare-earth ion at which the hydrogenic site observed here becomes apparent. A hydrogenic modification of the C_{3v} site can be obtained by a hydride ion substituting for one of the regular fluorine ions and a possible configuration is given in Fig. 10. The tetrahedral site line at

TABLE V. Frequencies, linewidths, and intensities of the local mode lines of a low-symmetry site in hydrogenated strontium-fluoride crystals containing 0.05 at.% of rare-earth ions recorded at 77°K.

Rare earth	Frequency (cm^{-1})	Linewidth (cm^{-1})	Frequency (cm^{-1})	Linewidth (cm^{-1})	Intensity relative to the lowest-frequency line	Frequency (cm^{-1})	Linewidth (cm^{-1})	Intensity relative to the lowest-frequency line
Dy	805.7 ± 0.8 [a]	3.3 ± 1.0	823.5 ± 0.7	2.8 + 0.5	0.7 ± 0.4	1278 ± 2 [a]	5.0 ± 1.5	0.5 ± 0.4
Ho	808.4 ± 0.9	3.2 ± 1.0	828.0 ± 0.9 [a]			1276.0 ± 1.6 [a]		
Y	811.0 ± 0.7	3.4 ± 0.5	831.3 ± 0.7	2.8 ± 0.5	1.5 ± 0.9	1266.0 ± 1.5	5.8 ± 1.0	0.8 ± 0.4
Er	811.3 ± 0.8 [a]	4.0 ± 1.0	831.8 ± 0.7 [a]	4.6 ± 1.0	1.4 ± 0.8	1275.6 ± 1.2	6.2 ± 0.5	0.9 ± 0.4
Tm	813.8 ± 0.8	4.1 ± 0.7	836.0 ± 0.7	3.6 ± 0.5	1.5 ± 0.6	1276.3 ± 1.2	5.4 ± 0.5	1.3 ± 0.6
Lu	816.6 ± 0.7	3.5 ± 0.5	839.2 ± 0.6	2.8 ± 0.5	1.3 ± 0.7	1276.3 ± 1.6	5.5 ± 0.6	1.0 ± 0.5

[a] In the same frequency region as other absorption lines.

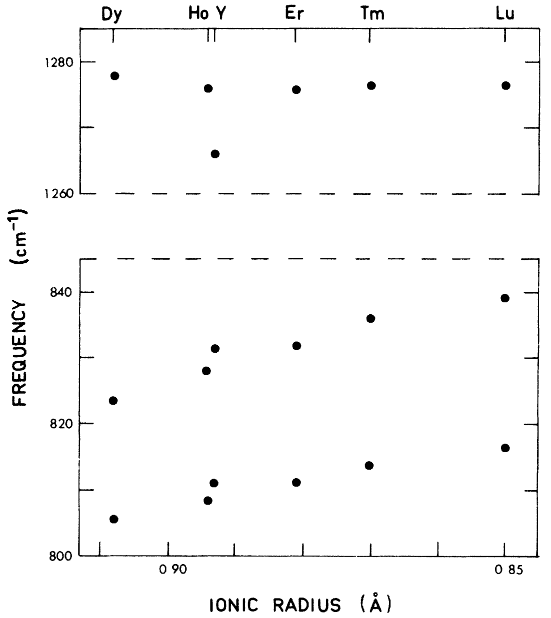

FIG. 9. Frequencies of the low-symmetry site local mode lines in hydrogenated strontium fluorides containing 0.05-at.% rare-earth ions, as a function of the trivalent rare-earth ion radius.

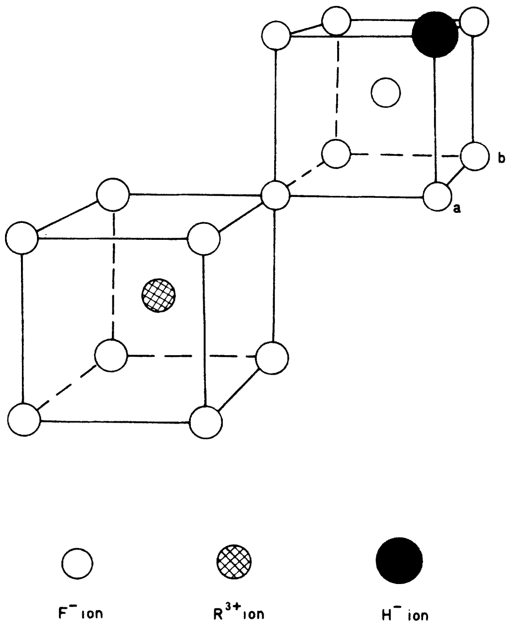

FIG. 10. Proposed model for the low-symmetry site. Other possible models are those having the substitutional hydride ion in the alternative positions *a* and *b*.

892.8 cm^{-1} is split into two lines by the interstitial fluoride ion. The more distant rare-earth ion shifts and splits the two lines into a total of three. The latter has a relatively small effect, as shown by the small frequency separation of the two lower-frequency lines, and by the small change in frequency of the lines with change in rare-earth ion.

E. Other hydride-ion sites

Several other hydrogenic lines were observed in hydrogenated crystals that have been stored at room temperature for several months. Representative spectra are shown in Fig. 11. From joint infrared and EPR studies at least two of these lines are associated with the rhombic R_2 site described in Sec. III C. It is not known which of the other local mode lines are also related to this site, since no positive correlation could be established for any of the remaining lines. The frequencies of the two lines that did show a correlation are listed in Table VI.

F. Ultraviolet-irradiation-induced sites

No extensive ultraviolet-irradiation studies were carried out, and the spectra for the few crystals that were irradiated are shown in Fig. 12. These results supplement those obtained in a preliminary study of the ultraviolet-irradiation sites by Le Heron.[13] The results of the combined studies are given in Table VII. Several new local mode lines appear on ultraviolet irradiation and are removed by warming the crystals to room temperature. These irradiation-induced lines have reduced intensities in the holmium, erbium, and lutecium crystals indicating that their sites are less favorable for rare-earth ions in the latter part of the series. The cerium and praseodymium spectra have special features. The 791-cm^{-1} cerium line at 77 °K was found to be split into two lines at 788.0 ± 1.2 and 791.7 ± 1.2 cm^{-1} at 4.2 °K. The praseodymium spectra have a doublet at 1231.0 and 1236.6 cm^{-1} in place of the single line observed in the other rare-earth crystals, and also have an additional line at 928.6 ± 1.0 cm^{-1}.

Three of the irradiation induced lines change systematically along the rare-earth series. With the spectra obtained, they did not correlate in intensity so cannot be assigned to only one site. The lowest- and highest-frequency lines occur at frequencies which are analogous to those found for ultraviolet-irradiated calcium-fluoride crystals containing gadolinium.

In earlier work Jones *et al.*[1] reported a vibronic line corresponding to 767 cm^{-1} for calcium-fluoride crystals containing gadolinium, but failed to observe any local mode lines corresponding to this in the infrared. In those measurements, the crystal was clamped to a copper block at 77 °K and sub-

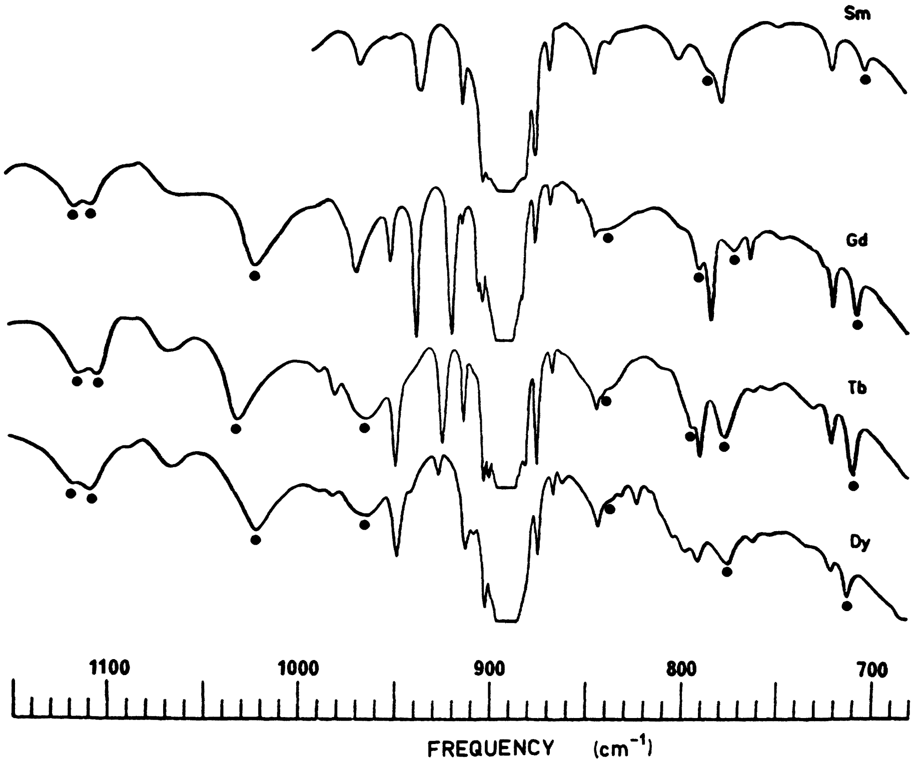

FIG. 11. 77 °K infrared spectra of hydrogenated strontium-fluoride crystals containing 0.05 at.% of rare-earth ions which have been stored for several months at room temperature. The new local mode lines are identified by ●.

TABLE VI. Frequencies at 77 °K of the two local mode lines that correlate in intensity with the rhombic R_2 site in hydrogenated strontium-fluoride crystals containing rare-earth ions.

Rare earth	I	II
Nd	699.0 ± 0.9	···
Sm	702.6 ± 1.0	783.0 ± 2.7
Gd	707.6 ± 1.2	790.1 ± 1.7
Tb	711.0 ± 1.7	794.5 ± 1.7
Dy	714.0 ± 1.2	···

TABLE VII. Frequencies (at 77 °K) of the ultraviolet irradiation lines in hydrogenated strontium-fluoride crystals containing rare-earth ions.

Rare earth	I	II	III	Source
La	786.8	···	1234.0	a
Ce	763.8 ± 1.3	~791	1231.9 ± 1.8	This work
Pr	761.1 ± 0.7	792.9 ± 0.7	1231.0 ± 1.0 1236.6 ± 1.0	This work
Nd	758.5 ± 0.7	798.0 ± 0.9	1236.1 ± 1.0	This work
Sm	754.5 ± 0.9	···	1239.0 ± 2.6	This work
Gd	752.5	787.3	1240.9	a
Tb	752.3	···	1242.1	a
Dy	751.6	793.8	1241.6	a
Ho	750.0	···	···	a
Er	749.7 ± 0.8	···	1242.5 ± 1.6	This work
Lu	747.6	···	···	a

[a] Reference 13.

jected to intense ultraviolet irradiation. The EPR studies of the calcium-fluoride rhombic R_3 site in this present work (Sec. III) show that this site is unstable above 100 °K. A 2-h ultraviolet irradiation of a crystal held at 77 °K by direct immersion in liquid nitrogen resulted in a 90% conversion of the hydrogenic C_{4v} site to the rhombic R_3 site, while a similar period of irradiation for a crystal at 85 °K clamped to a cold finger produced only 30% conversion. From this, it was realized that the earlier null result found by Jones *et al.*[1] was caused by the elevation of the crystal temperature above the stability regime of the rhombic R_3 site in calcium fluoride. When the crystal was weakly irradiated for periods of up to 10 h, and examined in the infrared it was found that the two local mode absorption lines characteristic of the hydrogenic C_{4v} site disappeared and two new local mode lines appeared. The sharp line at 768.5 cm^{-1} is in excellent agreement with the vibronic interval of 767 cm^{-1} in the gadolinium optical spectrum. The second line at 1326 cm^{-1} is broad with a linewidth of 15 cm^{-1}. Both lines disappear when the crystal is raised to room temperature for a few minutes and recooled.

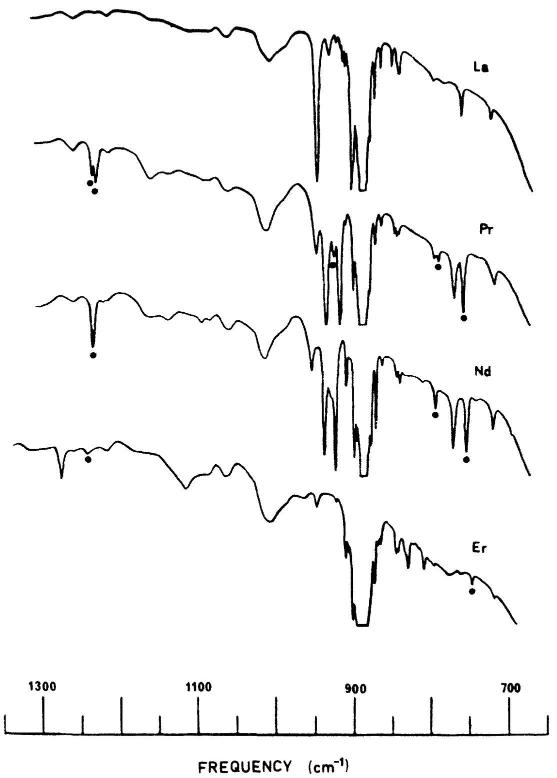

FIG. 12. 77 °K infrared spectra of ultraviolet irradiated (at 77 °K) hydrogenated strontium-fluoride crystals containing 0.05 at.% of rare-earth ions. The new local mode lines are identified by ●.

Ashburner and Newman[14] have performed similar irradiation experiments on calcium-fluoride crystals and found two additional absorption lines at 984.3 and 997.6 cm^{-1} which did not appear in our spectra. It is apparent that the particular sites produced by ultraviolet irradiation depend on the crystal temperature.

The highest-frequency irradiation induced line in strontium fluoride (Table VII) corresponds to the 1326-cm^{-1} line in calcium fluoride containing gadolinium. It varies little with the rare-earth ion and is assigned as the vibrational frequency of an isolated interstitial hydride ion, slightly perturbed by a distant rare-earth ion. By analogy with the calcium-fluoride results, the frequency of an isolated interstitial hydride ion in strontium fluoride would then be about 1220 cm^{-1}.

G. Hydride-ion sites in barium-fluoride crystals

Hydrogenated barium-fluoride crystals containing trivalent rare-earth ions were also examined in the infrared. The spectra show little similarity to those found for strontium fluoride. The spectra for the 0.05-at.% concentration crystals are given in Fig. 13. Only one line is markedly dependent

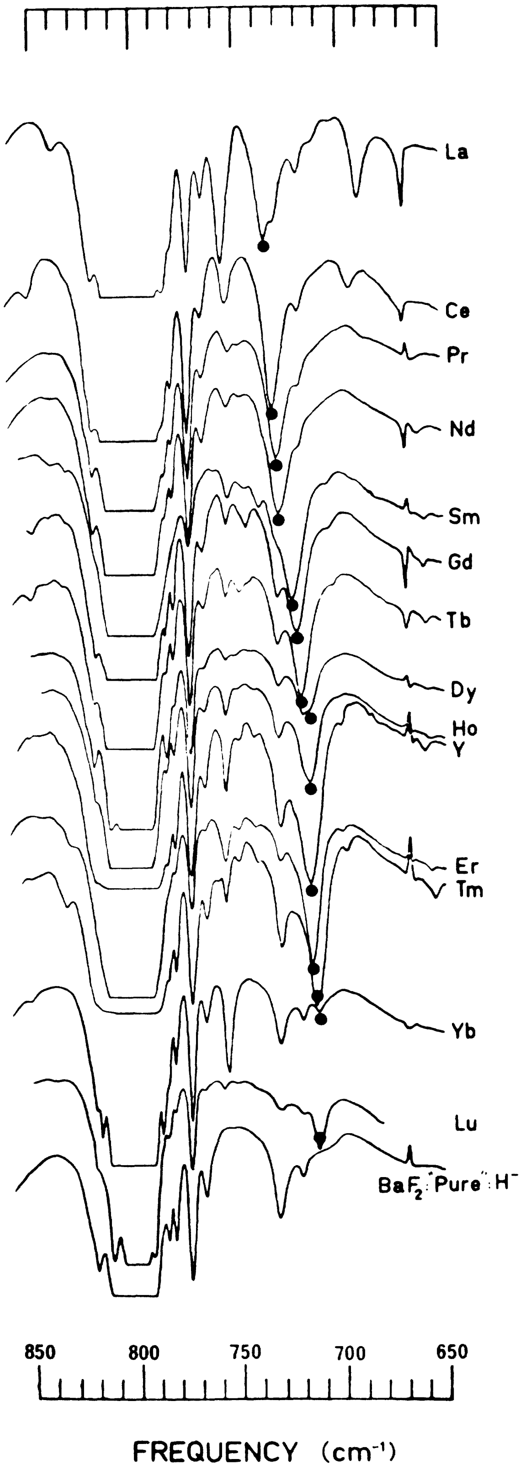

FIG. 13. Infrared spectra of hydrogenated barium-fluoride crystals containing 0.05 at.% of trivalent rare-earth ions recorded at 77 °K. The predominant rare-earth-dependent local mode line is identified by ●.

on the particular rare-earth ion present (Table VIII). It does not correlate in intensity with any other local mode lines in the spectra. Furthermore the only lines in the strontium-fluoride spectra showing any similarity to this line are the low-frequency irradiation-induced lines (Sec. IV F). The frequency of this barium-fluoride line is lower than that of the substitutional hydride ion site of tetrahedral symmetry which is present in all hydrogenated barium-fluoride crystals at 806.3 cm^{-1}.[6] Such a low frequency suggests that this line is associated with a modified substitutional hydride-ion site rather than an interstitial hydride-ion site as found for the other alkaline-earth fluorides. On ultraviolet irradiation new local mode lines appear.[15] Because of the complexity of these irradiation spectra, no details are presented in this paper.

Hydrogenated barium fluoride crystals containing either 0.05 or 0.3 at.% of trivalent uranium showed a more complex spectra than the crystals containing rare-earth ions. However, two local mode lines were observed at 849.3 ± 0.9 and 912.8 ± 1.1 cm^{-1} and these correlated in intensity in all the spectra measured. They almost completely disappeared after ultraviolet irradiation of the crystals. These two lines are tentatively assigned to the hydrogenic C_{4v} site. The existence of this site in uranium crystals and not in those containing rare earths is possible since the ionic radius of trivalent uranium is appreciably larger than those of any of the trivalent rare-earth ions and is sufficient to allow the formation of a stable fluorine ion C_{4v} site.[12] Kiel and Mims[16] have observed such

TABLE VIII. Frequencies and linewidths at 77 °K of the main rare-earth-dependent local mode line in hydrogenated barium-fluoride crystals containing 0.05 at.% of rare-earth ions.

Rare-earth ion	Frequency (cm^{-1})	Linewidth (cm^{-1})
La	736.8 ± 1.6	7.8 ± 1.0
Ce	733.2 ± 1.4 [a]	5.1 ± 1.0
Pr	730.9 ± 1.4 [a]	8.2 ± 0.5
Nd	730.7 ± 1.6 [a]	8.0 ± 1.0
Sm	724.6 ± 1.6 [a]	9.2 ± 1.0
Gd	722.2 ± 2.0 [a]	
Tb	720.0 ± 1.4 [a]	7.7 ± 0.8
Dy	717.2 ± 2.1 [a]	
Ho	716.6 ± 1.5	7.8 ± 0.8
Er	715.8 ± 1.4	6.2 ± 0.5
Tm	713.9 ± 1.5	5.4 ± 0.5
Yb	712.4 ± 2.1 [b]	
Lu	712.3 ± 1.5	5.9 ± 0.5

[a] Partially masked by other local mode lines.
[b] Not intense enough for linewidth measurements.

fluorine ion sites in barium-fluoride crystals containing uranium using EPR while barium-fluoride crystals containing cerium[7] or gadolinium show no such sites in their EPR spectra.

V. SUMMARY

This investigation of the infrared spectra of hydrogenated strontium-fluoride crystals containing trivalent rare-earth ions has established that the rare-earth–hydride-ion charge-compensation arrangements changes near holmium, and the change is to a different site from what would be expected from the EPR measurements made on the rare-earth–fluoride-ion sites.[12] In the strontium-fluoride crystals before hydrogenation, the trivalent rare-earth ions are in principally tetragonal symmetry fluoride-ion sites for rare-earth ions in the first part of the rare-earth series and in trigonal symmetry fluoride-ion sites in the latter part of the series. Our infrared measurements show that there are no trigonal symmetry hydride ion sites for rare-earth ions in the latter part of the series. The three infrared lines that are observed for the latter part of the series correlate in intensity and are, therefore, assigned to a lower symmetry site. EPR measurements would be helpful to elucidate the exact ion arrangement for this site.

The stability along the rare-earth series of the C_{4v} site is similar for both hydride and fluoride-ion charge compensation. EPR data show that the fluoride ion C_{4v} site becomes unstable between the rare earths gadolinium and erbium[12] in the series, while our infrared data show that the hydrogenic C_{4v} site is absent after holmium.

Brown *et al.*[12] relate the changeover of site to the relative ionic radii of the trivalent rare-earth ion and the divalent cations of the host lattice, using a model involving the contributions of the attractive Coulomb and the repulsive overlap potentials. In the strontium-fluoride crystals this model predicts a change over in the fluoride-ion sites from tetragonal to trigonal symmetry in the vicinity of dysprosium, in agreement with our hydrogenic site results. For barium-fluoride crystals, the changeover is predicted to occur around praseodymium in the rare-earth series. Our results show that the hydrogenic C_{4v} site is absent for all rare-earth ions in barium fluoride, although present for the larger trivalent uranium ion. Considering the approximations of the model, our results are in good qualitative agreement.

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