

resulting from the field is similar to that in a normal edge. If the field is more transverse, a branch of different functional form appears and the oscillations in $\Delta\alpha_T(\mathcal{E})$ occur on the opposite side of the threshold. The M_3 threshold electro-absorption is similar to that of the M_0 edge. Since all edges have different $\Delta\alpha(\mathcal{E})$ dependences on field orientation and photon energy, it should be possible to identify the nature of higher lying

direct optical transitions on the basis of the measurement of the electro-absorption effect.

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Coupling between H^- Localized Modes and Rare-Earth Ion Electronic States in Rare-Earth Trifluorides*

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Crystals of LaF_3 , CeF_3 , PrF_3 , and NdF_3 doped with hydrogen and deuterium have been studied spectroscopically. Two strong polarized fundamentals and their combinations have been observed in the infrared for both H^- and D^- . The fundamentals appear also polarized in the vibronic spectrum of doped NdF_3 coupled to several electronic transitions. Extra electronic lines appearing only in the doped crystals occur on the long-wavelength side of the usual rare-earth electronic transitions. From frequency differences, these extra levels are the parent states for the local mode vibronic transitions. The displacement of the extra electronic lines from the usual electronic transitions is mainly due to a changed crystalline field and covalency arising from the replacement of F by H, and is greater at higher levels. In addition the extra electronic levels have slightly different frequencies for hydrogenated and deuterated crystals. This isotope shift depends in both magnitude and sign on the particular electronic level and ranges from 0.5 cm^{-1} (for transitions to ${}^4F_{3/2}$) to -2.0 cm^{-1} (for transitions to ${}^4F_{7/2}$). This effect is accounted for by a large difference in zero-point amplitude for H^- and D^- localized modes which, through the electron-vibration interaction, perturbs each electronic level to a different extent.

INTRODUCTION

THE infrared absorption due to localized modes of H^- defects in crystals¹⁻⁴ as well as the electronic transitions of the U center in the ultraviolet⁵ are well known. Because the concentrations of H^- attainable in certain ionic crystals in which the H^- replaces the anion are relatively large (of the order of 0.01%) it is possible to study the coupling of the localized H^- ion vibrations with the electronic states of rare-earth ions in crystals. Our study is concerned with such coupling for localized H^- and D^- modes in rare-earth trifluorides, chiefly NdF_3 .

The coupling is manifested in several ways: (1) as a shift in the electronic levels of the rare-earth ion in the changed environment due to the H^- , (2) as an isotope effect for these shifted lines, and (3) as vibronic transi-

tions involving the absorption of a photon by the rare-earth ion accompanied by the creation of one localized phonon. We also present the results of polarized low-temperature infrared absorption by the H^- and D^- localized vibrations.

The rare-earth trifluorides are experimentally suitable for our studies because of the readiness with which they can be heavily doped with hydrogen and so display observable optical effects. However, they suffer from certain difficulties which limit the extent one can at present push the theoretical analysis of the results. Various studies involving rare-earth trifluorides suffer from a lack of agreement as to the crystal structure. Two slightly different crystal structures have been proposed for LaF_3 from x-ray analysis, one involving two molecules per unit cell with the rare-earth ions at D_{3h} sites,⁶ and the other involving six molecules per unit cell with rare-earth ions at C_{2v} sites.⁷ Nuclear magnetic resonance studies⁸ on pure LaF_3 single crystals have recently shown that there are six magnetically different La sites with site symmetry either C_s or C_{2h} , and based on these results a third crystal structure has

* Some of the results of this paper were presented at the September 1965 meeting of the American Physical Society. See APS Bulletin 10, 686 (1965).

¹ G. Schaefer, J. Phys. Chem. Solids 12, 233 (1960).

² B. Fritz, J. Phys. Chem. Solids 23, 375 (1962).

³ B. Fritz, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965).

⁴ R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. Roy. Soc. (London) A289, 1 (1965).

⁵ R. W. Pohl, Proc. Phys. Soc. (London) 49, 3 (1937).

⁶ K. Schlyter, Arkiv Kemi 5, 73 (1952).

⁷ I. Oftedal, Z. Krist. 72, 239 (1929); 78, 462 (1931).

⁸ L. O. Andersson and W. G. Proctor (to be published).

TABLE I. Fundamental frequencies, polarizations, relative intensities, and linewidths of the infrared-absorption lines of the local modes of H⁻ in rare-earth trifluorides at 4.2°K.

Polarization	LaF ₃			CeF ₃ (cm ⁻¹)	PrF ₃ (cm ⁻¹)	NdF ₃ (cm ⁻¹)
	Frequency (cm ⁻¹)	Relative intensity	Linewidth (cm ⁻¹)			
σ	772.2±0.2	12	<1		801.5±1	816.2±0.2 <i>A</i>
π	817.5±0.2	29 ^a	<0.8	842.5±1	868.7±0.2	883.2±0.2 <i>B</i>
σ/π	937.5±0.5	14/5.4	7	^b	958.5±1.0	969.0±1.0 <i>C</i>
σ	1118.0±0.5	2	1.4		1123.1±0.5	1128.5±1.0 <i>D</i>
π	1129.0±1.0	14	10	^b	1147 ±2	1159.0±1.0 <i>E</i>
σ	1167.8±0.2	100	4	1171.5±1	1182.6±0.3	1197.3±0.2 <i>F</i>

^a Intensity of π line reduced due to it being recorded with spectrophotometer under limiting resolution conditions.

^b These bands did not appear. Presumably the corresponding site is less favorable in CeF₃.

been proposed.⁸ Electron paramagnetic resonance studies⁹ on LaF₃ doped with several different rare earths have indicated a low symmetry site for the rare-earth ion, but with principal axes (except for gadolinium) not along symmetry determined directions of the C_{2v} site in the proposed hexamolecular structure. Electronic spectra of Pr³⁺, Nd³⁺, and Er³⁺ in LaF₃ are not consistent with any single-ion site symmetry. The Pr³⁺ spectrum¹⁰ is consistent with a C_{2v} site, the Nd³⁺ spectrum¹¹ shows some lines which are completely polarized, which is incompatible with C_{2v} or any other orthorhombic or lower symmetry, and the Er³⁺ spectrum¹² displays some partially and some completely polarized lines which were postulated as indicating a symmetry slightly distorted from a trigonal site such as D_{3h}.

The location and symmetry of the fluorine ion sites suffers a similar inconclusiveness awaiting further structural analysis. The bimolecular unit cell has two fluorine sites at D_{3h} sites and four at C_{3v}; the hexamolecular unit cell has three types of fluorine sites, 12 at C₃, four at C_{3h}, and two at D_{3h}.

It is possible that some of the inconsistencies are accounted for in terms of distortions of the lattice in the vicinity of rare-earth impurity ions. The presence of hydrogen impurity may also produce distortions.

EXPERIMENTAL TECHNIQUES

Rare-earth trifluoride crystals were first heated under high vacuum to 500°C, in the presence of aluminum metal. Hydrogen or deuterium gas was then introduced at pressures up to two thirds of an atmosphere and the temperature raised to 800°C for 16 h. After cooling, excess aluminum was removed and the crystals polished.

This method of introducing hydrogen and deuterium was first applied to calcium fluoride by Hall and

⁹ J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) **78**, 1353 (1961).

¹⁰ E. Y. Wong, O. M. Stafsudd, and D. R. Johnston, J. Chem. Phys. **39**, 786 (1963).

¹¹ E. Y. Wong, O. M. Stafsudd, and D. R. Johnston, Phys. Rev. **131**, 990 (1963).

¹² W. F. Krupke and J. B. Gruber, J. Chem. Phys. **39**, 1024 (1963).

Schumacher¹³ and works equally well for rare-earth trifluoride crystals.

The concentration of impurity introduced into the crystal as estimated from the intensity of the infrared absorption is 4×10¹⁸ ions/cm³.

Infrared measurements were made in the 400–4000 cm⁻¹ range with a Beckman IR9 spectrophotometer. Low-temperature spectra were obtained by using a metal Dewar designed to operate in conjunction with the Beckman KBr lens microbeam condenser and the AgCl polarizer. The crystals were cooled by thermal contact with a copper block and reached a temperature somewhat higher than that of the refrigerant.

The visible spectrum of the PrF₃ and NdF₃ crystals were photographed at 4°K on the 21-ft concave grating spectrograph at UCLA. For measurements requiring less dispersion, further plates were taken on a Bausch and Lomb dual-grating spectrograph. The crystals were immersed directly in liquid helium contained in a double glass Dewar system. Wavelengths were measured to better than 0.2 Å.

INFRARED ABSORPTION SPECTRUM

The Main Lines

The infrared absorption spectrum of hydrogen and deuterium in lanthanum fluoride consists of fifteen lines

TABLE II. Harmonic and combination infrared-absorption lines of the local modes of H⁻ in 16-mm-thick LaF₃ near 4.2°K.

Polarization	Frequency (cm ⁻¹)	Relative intensity	Line width	Assignment
σ/π	1542.3±0.5	16/26	4.8	2×772.2
σ	1570.5±0.5	32	11	?
π	1624.5±0.5	4	4.5	2×817.5
σ	1707 ±1	57	24	772.2+937.5
π	1861.0±0.5	16	19	2×937.5
σ	1985.0±0.5	100	4.6	817.5+1167.8
σ	2236	4	6	2×1118 ?
π	2245	23	34	2×1129 ?
σ	2330.5±0.5	410 ^a	8.0	2×1167.8

^a The intensity of this line is 1/20 of the intensity of line *F* in Table I.

¹³ J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

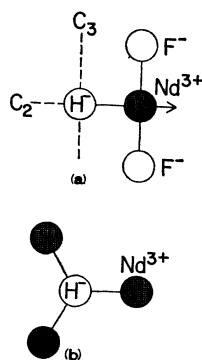


FIG. 1. (a) Proposed location of the H^- impurity at a F^- site of D_3 symmetry. The Nd^{3+} site is located on a C_3 axis in the bimolecular cell model, and is displaced along the twofold axis (in the direction of the arrow) in the hexamolecular cell model. The other ions obtained by C_3 operations about an axis through the H^- site are not drawn. The F^- ions shown are in the plane of the C_3 and C_2 axes which go through the H^- site. To obtain our proposed D_3 symmetry at the H^- site the F^- ions shown must be rotated about the C_2 axes somewhat, so that a modification of the originally proposed x-ray structure results. (b) View of H^- site looking down C_3 axis. F^- ions are not shown.

whose frequencies, relative intensities, and linewidths are given in Tables I, II, and III. The corresponding frequencies for CeF_3 , PrF_3 , and NdF_3 are also shown in Table I. They display an increase from those of LaF_3 as a consequence of the decrease of the lattice parameters from La to Nd. The overtone and combination data for the H^- local mode are incomplete for these three fluorides, as the rare earths have a strong electronic absorption in the 2000-cm^{-1} region arising from the transition to the first-excited multiplet of these ions ($^2F_{5/2} \rightarrow ^2F_{7/2}$ for Ce^{3+} , $^3H_4 \rightarrow ^3H_5$ for Pr^{3+} , and $^4I_{9/2} \rightarrow ^4I_{11/2}$ for Nd^{3+}) which prevents observations of all the harmonics and combinations. Strong lattice absorption setting in below 700 cm^{-1} also prevents observation of the lower strong deuterium fundamental, but this frequency can be deduced from the appropriate combination (see Table III).

Owing to experimental limitations it was not possible to measure the infrared absorption of crystals thicker than 16 mm, so no third harmonics were observed.

When hydrogen goes into the rare-earth trifluoride crystals we assume that most, if not all, of it enters as H^- replacing F^- . The location of H^- at F^- sites has been established in the alkali halides (U centers) and in the alkaline-earth fluorides. The infrared spectra observed here are consistent with this type of defect. The lines are far too strong to be due to neutral hydrogen atoms and they show the expected $\sqrt{2}$ ratio between hydrogen and deuterium frequencies. Furthermore, the frequencies are roughly the values obtained when lattice mode frequencies are multiplied by a factor of the square root of the fluorine-to-hydrogen mass ratio, which is consistent with the substitution of a hydrogen for a fluorine in the LaF_3 lattice. We do not wish to imply by this argument that such an exact relationship

TABLE III. Frequencies and polarizations of the infrared-absorption lines of the D_3 site local mode of hydrogen and deuterium in rare-earth trifluorides at 77°K .

	LaF_3		PrF_3		NdF_3	
	H^-	D^-	H^-	D^-	H^-	D^-
$A\sigma$	1168	833	1183	844	1194	853
$B\pi$	816	584 ^a	866	622 ^a	882	632 ^a
$(A+B)\sigma$	1983	1417	...	1466	...	1485
$(2A)\sigma$	2330	1663	...	1686	2386	1705
$A(H)/A(D)$	1.40		1.40		1.40	
$B(H)/B(D)$	1.40		1.39		1.40	

^a These frequencies inferred from $(A+B) - A$.

should exist between the local mode and lattice frequencies, but merely that the force constants for the H^- ion are much closer to those acting on F^- than the values they would be if the hydrogen went in as H^+ .

The number of lines observed requires that the hydrogen be entering into more than one of the possible fluorine sites.

Site of Impurity Ions

From the fact that the two strongest H^- infrared lines at 1168 cm^{-1} and 817 cm^{-1} in LaF_3 and their counterparts in CeF_3 , PrF_3 , and NdF_3 have a combination line, one concludes that these lines are due to H^- vibrations at the same site, which is preferentially occupied. The appearance of the corresponding combination for D^- confirms this conclusion.

The polarization of the fundamentals, one overtone, and the combination line enables a determination of the site symmetry of the hydrogen by the following reasoning: The line at 817 cm^{-1} has π polarization and an effectively zero second harmonic. This restricts consideration to those point groups for which Z is a basis for

TABLE IV. Frequencies of the lattice combination bands observed near the polarized 1168-cm^{-1} H^- local mode fundamental of LaF_3 at 4.2°K .

Frequency (cm^{-1})	Separation from 1170 cm^{-1}	Infrared data ^a	Raman data ^a
		(room temperature) (cm^{-1})	(room temperature) (cm^{-1})
1225	55		
1240	70		75
1300	130		
1305	135		
1320	150		
1325	155		
1340	170		
1360	190	185	
1400	230	208	
1420	250		
1450	280	275	292
1470	300		310
1495	325	358	365
1570?	400		392

^a Taken from Ref. 14.

TABLE V. Extra electronic lines observed in hydrogenated and deuterated praseodymium fluoride at 4.2°K.

Level	Hydrogenated PrF ₃ line (cm ⁻¹)	Deuterated PrF ₃ line (cm ⁻¹)	Isotope shift (cm ⁻¹)	Corresponding main line in pure PrF ₃ (cm ⁻¹)	H ⁻ to pure line covalency shift (negative) (cm ⁻¹)
¹ D ₂	16818.8±0.15	16819.7±0.15	0.70±0.08	16871.3±0.05	52.5±0.15
	16851.3±0.1	16851.6±0.3	0.33±0.25*	16902.1±0.15	51.8±0.2
³ P ₀	20878.2±0.1	20879.4±0.1	1.11±0.12	20923.2±0.2	45.0±0.25
³ P ₁	21368.6±0.05	21369.7±0.1	1.03±0.1	21466.6±0.1	98.1±0.1
	21375.6±0.15	21377.3±0.1	1.55±0.18	21473.0±0.05	97.4±0.2
	21398.9±0.05	21400.2±0.2	1.12±0.23	21522.1±0.25	123.2±0.25

* Large error due to overlap with a weak line present in both pure and doped PrF₃.

a one-dimensional representation other than the identity Γ_1 , but having the property that $\Gamma_z^2 = \Gamma_1$. Of these possible site groups we consider only those for which $\Gamma_{x,y} \times \Gamma_z = \Gamma_{x,y}$ since a σ and a π line appear as a σ combination. This rules out D_{3h} , C_{3h} , and C_s . Since the second harmonic of the σ line also has σ polarization we require in addition that the site group have the property that the symmetric product $[\Gamma_{x,y}]^2$ does not contain Γ_z . This eliminates D_{2d} and S_4 . The only point groups satisfying these three criteria are the dihedral groups D_2 , D_3 , D_4 , and D_6 . As stated in the introduction, there are no F⁻ sites having any of these symmetries according to either of the proposed x-ray crystal structures. However, one of the allowed site symmetries is D_{3h} in either structure. An F⁻ ion lying on a C_3 axis and having three nearest neighbor rare-earth ions in the xy plane containing this F⁻ ion, occupies a D_{3h} site (see Fig. 1). An H⁻ ion replacing the F⁻ ion at this site can have D_3 symmetry if the reflections in the forementioned xy plane are destroyed by a slight twisting about each of the three twofold axes passing through the H⁻ and a rare-earth ion. None of the other dihedral groups can be made compatible with any of the F⁻ sites. Furthermore, the F⁻ site selected above as the H⁻ site has the shortest F-La distance,¹⁴ 2.35 Å. This, together with the selective occupancy of the H⁻ in this site, makes reasonable the observation that only the infrared frequencies of this site appear in the vibronic spectrum, as will be shown below.

One can suggest that of the remaining four infrared fundamental frequencies observed, three could be associated with a C_s symmetry site in which the reflection plane is vertical, which is consistent with the hexamolecular x-ray crystal structure. These lines (*A*, *C*, *E*) of Table I are of roughly equal intensity; about one third of those just discussed. Harmonics and combinations are observed as also shown in Table II. By applying similar arguments to above, the observed polarizations can be accounted for in the following way: Line *A* is associated with H⁻ motion perpendicular to the vertical reflection plane. The other two (*C*, *E*)

correspond to H⁻ motion in the reflection plane with principal axes not along nor perpendicular to the crystal *Z* axis (optic axis), and consequently can be partially polarized. This is definitely true for one of the lines, while the other is almost purely polarized. As the observed lines do not display completely the polarization behavior required, and, as the combinations (which should be unpolarized) are markedly stronger in π polarization, this interpretation of the lines as arising from H⁻ ions in C_s site symmetry is tentative.

No explanation can be offered to account for the one remaining relatively weak line (*D*).

Satellite Lines

Weak σ -polarized broad bands are observed in the vicinity of the strong σ -polarized line which occurs at 1167.8 cm⁻¹ in hydrogenated LaF₃. These are assigned to combination bands whose frequencies are the sum of the localized mode and lattice band modes. Similar bands have been observed in the alkali halides^{1,2,15} and the alkaline-earth fluorides.⁴ The peaks of these bands are tabulated in Table IV and their separations from the 1167.8-cm⁻¹ local mode frequency yield frequencies of singularities in the lattice spectrum of LaF₃. The infrared-active and Raman-active lattice frequencies⁴ of pure LaF₃ are also shown for comparison.

The observed spectrum reflects the single phonon density of states of the LaF₃ lattice spectrum weighted by a $1/\omega$ frequency factor, where ω is the separation of the sideband from the main line.⁴ No attempt has been made to fit the data in view of the complexity of the LaF₃ lattice. The data may be regarded solely as giving information about the density of states.

ELECTRONIC ABSORPTION SPECTRUM

Covalency Effect

After hydrogenation, both PrF₃ and NdF₃ display lines at slightly longer wavelengths than the usual electronic transitions, and these are tabulated in Tables V and VI, together with their frequency separation from

¹⁴ H. H. Caspers, R. A. Buchanan, and H. R. Marlin, J. Chem. Phys. 41, 94 (1964).

¹⁵ S. S. Mitra and Y. Brada, Phys. Letters 17, 19 (1965).

TABLE VI. Extra electronic lines observed in hydrogenated and deuterated neodymium fluoride at 4.2°K.

Level	Hydrogenated NdF ₃ line (cm ⁻¹)	Deuterated NdF ₃ line (cm ⁻¹)	Isotope shift (cm ⁻¹)	Corresponding main line in pure NdF ₃ (cm ⁻¹)	H ⁻ to pure line covalency shift (negative) (cm ⁻¹)	Covalency shift (negative) of <i>J</i> level (calc.)
⁴ F _{3/2}	11580.7±0.05	11581.1±0.1	0.49±0.03	11595.3±0.05	14.6±0.1	14.4
	11629.8±0.1	11630.3±0.05	0.50±0.13	11643.5±0.05	13.7±0.15	
⁴ F _{5/2}	12580.7±0.05	12581.5±0.05	0.86±0.07	12595.8±0.1	15.1±0.1	13.2
	...	12598.3±0.25 ^a	...	12610.8±0.1	12.5±0.3 ^b	
	...	12610.6±0.3 ^a	...	12623.2±0.15	12.6±0.5 ^b	
⁴ F _{7/2}	13497.2±0.05	13495.1±0.05	-2.03±0.08	13513.3±0.1	16.1±0.15	15.5
	13577.0±0.25 ^c	13577.9±1 ^d	...	13596.1±0.1	19.1±0.3	
⁴ S _{3/2}	13703.1±0.2 ^c	13718.7±0.1	15.6±0.25	15.6±0.25
	13708.6±0.2 ^c	13710.0±1 ^d	...	13723.4±0.1	14.8±0.25	
⁴ F _{9/2}	14826.1±0.1	14826.8±0.1	0.65±0.14	14839.4±0.15	13.3±0.15	16.4
² H _{11/2}	15990.1±0.1	15990.7±0.15	0.56±0.19	15997.4±0.05	7.3±0.15	17.7
⁴ G _{5/2}	17256.5±0.1	17257.2±0.1	0.72±0.13	17304.9±0.15	48.4±0.2	26.7±0.15
	17285.6±0.1	17286.0±0.1	0.40±0.16	17312.3±0.1	25.7±0.15	
² G _{7/2}	17341.2±0.3 ^c	17341.7±0.25 ^a	...	17366.5±0.4	26.3±0.15	
⁴ G _{7/2}	19113.2±0.1	19113.7±0.1	0.47±0.11	19143.2±0.1	30.0±0.15	22.8
	19200.1±0.2 ^e	19200.1±0.05 ^e	0.02±0.2	19231.5±0.8	31.4±0.9	
	19214.4±0.3 ^e	19214.4±0.15 ^e	-0.03±0.3	19254.6±0.4	40.2±0.5	
² K _{15/2}	21135.8±0.1 ^e	21135.8±0.05 ^e	0.07±0.08	21153.5±0.2	17.7±0.2	17.7±0.2
	+ ² G _{9/2}					
² P _{1/2}	23439.1±0.1	23439.7±0.05	0.60±0.09	23470.7±0.05	31.6±0.1	28.4
² D _{5/2}	23952.4±0.2	23953.1±0.1	0.76±0.19	23981.0±0.1	28.6±0.2	28.0

^a Electronic line not seen directly, but inferred from position of associated D⁻ local mode vibronic.

^b D⁻ to pure line covalency shift.

^c Electronic line not seen directly, but inferred from position of associated H⁻ local mode vibronic.

^d D⁻ electronic lines inferred with assumption of 632 cm⁻¹ and 853 cm⁻¹ separation from the D⁻ vibronic.

^e Assignment to H⁻ or D⁻ lines tentative as isotope effect effectively zero; lines may be due to other impurities.

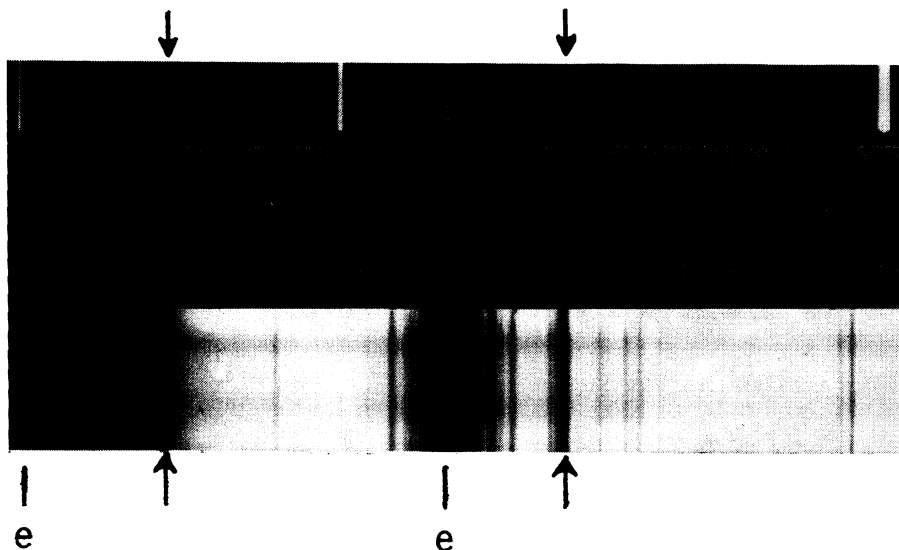
the corresponding main line. It was not possible to observe all the extra electronic lines of a group due to overlapping but, in general, only the lowest extra line could be easily observed. Some of the obscured lines could be inferred from the vibronic spectrum and are also shown in the table.

From a comparison of the frequencies of (a) local mode vibronic lines (described below), (b) local modes in the infrared, and (c) the extra electronic lines, it is evident that these electronic lines are parents for the local mode vibronics and so must arise from transitions between electronic states of the rare earths situated in a site where there is one nearest neighbor hydride ion. The shift of these extra electronic lines from those of the undoped crystal is a consequence of this changed environment around the rare earth due to the replacement of a fluoride ion by a hydride ion. As the local mode vibronics observed correspond to the infrared local mode lines attributed to a D₃ site symmetry this hydride ion occupies one of the fluoride sites shown in Fig. 1. Such a substitution can affect the energy levels in two ways: (1) through an altered crystal field acting on the rare-earth ion and (2) through a change in the covalent bonding of the rare-earth ion to its neighbors,

arising from the different ionic radius and electro-negativity of a hydride ion as compared to a fluoride ion.

The first mechanism appears to be smaller than the second, since (a) the shift in electronic levels is approximately constant within a given multiplet of levels, as seen from the sixth column of Tables V and VI (a large crystal field change would cause markedly different shifts for the different levels of a given multiplet); and (b) the shift increases for higher energy multiplets. All *J* multiplets are seen to have crystalline Stark levels shifted to lower energy relative to the ground level. The size of the shifts vary between about 50 and 100 cm⁻¹ depending on the observed *J* level in PrF₃ and vary between approximately 13 and 34 cm⁻¹ for the observed *J* multiplets in NdF₃. In each case for which more than one crystalline level per *J* level can be observed, the shift is roughly constant within a given *J* multiplet. The mean derivation of the individual observed levels from the average shift for each *J* level when averaged over the different *J* levels is 5.6% for PrF₃ and 12.4% for NdF₃. These figures can be taken as a rough measure of the relative effect of the changed crystalline field to that of the changed covalency. In other words the shifts are primarily due to a changed

FIG. 2. Spectrogram showing transitions to ${}^4F_{3/2}$ in NdF_3 at 4.2°K. The upper spectrum shows hydrogen-doped NdF_3 0.25 mm thick, and the lower shows deuterium-doped NdF_3 0.5 mm thick. The lines marked by arrows occur only in the doped crystals, and display the ordinary positive isotope shift, while all other lines are present in both pure and doped crystals. The two strong lines (e) are the normal electronic transitions, and the weak ones are presumably due to imperfections other than hydrogen or deuterium.



covalency and only secondarily due to a changed crystalline field. This conclusion is also reasonable in view of the fact that the shifts are of the same order of magnitude as the separation of crystalline Stark levels within a J multiplet in the unhydrogenated crystal. Thus the *difference* in the crystalline fields when a single H^- replaces an F^- cannot be responsible for such relatively large shifts.

A measure of the change in covalency caused by the hydride ion impurity could be obtained by determining the center of gravity of the new multiplets, and re-diagonalizing the energy matrices to give the change in the Slater integrals F_2 , F_4 , and F_6 and the spin-orbit parameter ζ . From our results, the center of gravity of each multiplet cannot be determined for more than one or two cases, so instead the lowest level of each multiplet was chosen as representative of the center of gravity. This approximation is justified under the assumption of a zero crystal field change. A first-order Taylor-series expansion method¹⁶ for determining the change in the four parameters F_2 , F_4 , and F_6 , and ζ was applied to eight multiplet levels of NdF_3 using the experimentally observed shift in place of the difference between calculated and observed energies, with the additional restriction that the changes in the F_k be proportional to their initial values given by Caspers *et al.*¹⁷ with a single adjustable constant of proportionality and the corresponding proportional change in ζ be one half¹⁸ that in the F_k . The derivatives previously tabulated¹⁶ were utilized and the parameter shifts are found to be $\Delta F_2 = -0.444$, $\Delta F_4 = -0.0619$, $\Delta F_6 = -0.0073$, and $\Delta \zeta = -0.579$. These correspond to a 0.13% decrease in F_k parameters; the smallness of the effect follows in

part from the fact that only one atom of the five surrounding the rare earth is substituted. The parameter shifts account for the observed shifts of the eight multiplet levels to within a mean deviation of 21% of the mean experimental separation. The calculated shifts for each J level used in adjusting one parameter are shown on the last column of Table VI. Obviously better agreement could be obtained by allowing all F_k and ζ to vary independently, but as the initial set of parameters¹⁷ used cannot fit the undoped crystal spectrum to better than 20 cm^{-1} , such a refinement in computing the shifts obtained by hydrogenation is unjustified, particularly since the shift in the center of gravity of each multiplet is not precisely known.

The Isotope Shift

Corresponding deuterated crystals of PrF_3 and NdF_3 also show extra electronic lines whose frequencies are slightly different from those produced by hydrogenation. Crystals heated in a 1:1 hydrogen-deuterium atmosphere display both lines. This isotope shift is shown in Tables V and VI for the various levels of Pr and Nd. Figures 2 and 3 are typical spectrograms for the ${}^4F_{3/2}$ and ${}^4F_{7/2}$ levels of NdF_3 .

The isotope effect arises through the coupling of the local mode vibration to the electronic states; the widely different amplitude for the hydrogen and the deuterium ion causes a different perturbation of the parent electronic state.

The appearance of vibronic spectra and isotope shifts depend on the electron-phonon interaction V_{ev} , which arises from a modulation of the crystalline field at the rare-earth $4f$ electrons during the vibrational motion. The interaction has the form

$$V_{ev} = \sum f_i^\alpha Q_i^\alpha + \sum g_{ij}^{\alpha\beta} Q_i^\alpha Q_j^\beta, \quad (1)$$

¹⁶ E. Y. Wong, J. Chem. Phys. 35, 544 (1961).

¹⁷ H. H. Caspers, H. E. Rast, and R. A. Buchanan, J. Chem. Phys. 43, 3214 (1965).

¹⁸ E. Y. Wong and I. Richman, J. Chem. Phys. 36, 1889 (1962); 37, 2498 (1962).

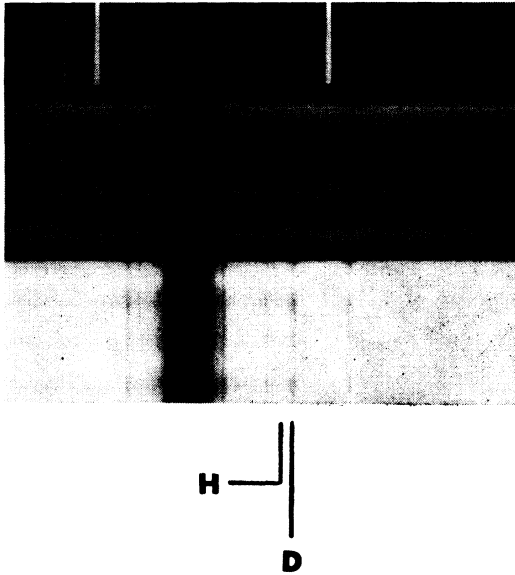


FIG. 3. Spectrogram showing transitions to the lowest crystalline Stark level of ${}^4F_{7/2}$ in NdF_3 at 4.2°K . The upper spectrum shows hydrogen-doped NdF_3 0.25 mm thick, and the lower shows deuterium-doped NdF_3 0.5 mm thick. The lines marked by arrows occur only in the doped crystals and display a negative isotope shift, while all other lines are present in both pure and doped crystals. The strong line is the normal electronic transition, and the weak ones are presumably due to imperfections other than hydrogen or deuterium.

where the Q are normal coordinates of the lattice and the f and g are functions of the electronic coordinates of the $4f$ electrons. We are particularly interested in those terms of V_{ev} which are due to the local modes of the H^- or D^- ion near to a rare-earth ion. The normal coordinates for the local modes are then, to a good approximation, simply ΔX , ΔY , and ΔZ , the displacements of the hydride ion from equilibrium. This follows from the small mass of H^- or D^- compared to the other atoms of the crystal. In a D_3 site ΔX , ΔY will be degenerate. In the Appendix the form of the even-degree g terms accompanying the terms $(\Delta X)^2$, $(\Delta Y)^2$, and $(\Delta Z)^2$ is presented for a point-ion model with the hydride-ion equilibrium position along the y axis from the rare-earth ion. The point-charge model no doubt leads to incorrect magnitudes for the coefficients of the angular dependent parts; nevertheless the model permits certain rough estimates which are of interest.

The electron-phonon interaction is responsible for a shift in each electronic level of a rare-earth ion. All the modes of the lattice contribute to this shift. However, when a rare-earth ion is near an H^- ion it has a different shift for each level than when it is near a D^- ion at the same site. We assume that the lattice modes are unaffected by whether H^- or D^- is present since both of the latter have local mode frequencies well above the highest optical branch of the crystal. Thus the lattice modes contribute equally to the electronic level shift for both H^- and D^- nearest neighbor. Hence we

shall ignore all lattice-mode contributions to the shift. Furthermore, there should be no temperature dependence of the H^- to D^- shift in the electronic levels, since the energies of the local modes are large compared with kT for the temperature range of interest.

The contribution of the first-degree terms in second-order perturbation are at least an order of magnitude smaller than the second-degree terms in first order. Second-order terms of the form

$$\langle uv_{n=1}(\Delta X) | f\Delta X | uv_{n=0}(\Delta X) \rangle^2 / \hbar\omega = \langle f \rangle^2 / 2m\omega^2$$

do not contribute at all to the observed isotope shift, since the force constant $m\omega^2 = k$ is the same for both H^- and D^- . However, if u_1 and u_2 are electronic eigenfunctions for two nearly degenerate crystalline Stark levels separated by energy E_{21} , one has approximately

$$\sum_{i=1}^3 \frac{\langle u_2 v_{n=1} | f_i \Delta X_i | u_1 v_{n=0} \rangle^2}{E_{21} + \hbar\omega_i} \approx F^2 \sum \frac{V_c^2 (\Delta X_i / r)^2}{E_{21} + \hbar\omega_i}, \quad (2)$$

where v_n is the local ΔX_i -mode vibrational wave function with n quanta of excitation (taken as harmonic oscillator functions), $\hbar\omega$ is the local ΔX -mode vibrational energy above zero point, V_c is the order of magnitude of the crystalline potential seen by a $4f$ electron, F is that fraction of V_c due to a single nearest neighbor ion ($F \approx \frac{1}{2}$), and r^2 is the mean square $4f$ radius.

The order of magnitude of the second-degree term in first order is given by

$$\sum_{i=1}^3 \langle uv_{n=0} | g_i (\Delta X_i)^2 | uv_{n=0} \rangle \approx F \sum_i V_c (\Delta X_i / r)^2. \quad (3)$$

Thus the ratio of the two contributions (3) and (2) to the shift of a level is of the order of

$$(E_{21} + \hbar\omega) / F V_c \approx (1/F)(1 + \hbar\omega / V_c) \approx 50,$$

although the actual ratio will vary considerably from level to level.

The relative H^- to D^- shift in each level can turn out to be either positive or negative, depending on the sign of the expectation value $\langle g \rangle$ of the electronic contribution to the electron-phonon interaction (3) for the particular electronic state involved. This accounts for the fact that one of the ${}^4F_{7/2}$ levels (see Table VI) is responsible for a negative shift relative to the usual order in all other observed cases. Presumably if more of the higher crystalline Stark levels of a J manifold could be observed, more examples of such reversals might be seen.

The isotope shift can be calculated once a set of eigenfunctions for the rare-earth ion in the crystalline field are known using a Hamiltonian such as in the Appendix. The uncertainty about the crystal structure and site symmetry make it unprofitable to attempt to determine crystalline field parameters. Furthermore, the identification of the energy levels necessary for such a

determination is hindered by lack of polarization and by the large number of crystal field parameters involved (nine for C_{2v}). Other hosts such as NdCl_3 may be more favorable for calculation.

We have, therefore, to confine our calculations to order-of-magnitude estimates of the expected size of the observed isotope effect. The mean-square displacement of the H^- ion is $\langle \Delta X \rangle^2 = \hbar/2m\omega = 2.82 \times 10^{-18} \text{ cm}^2$ for the 1194-cm^{-1} vibration, and $\langle \Delta Z \rangle^2 / \langle \Delta X \rangle^2 = 1194/882 = 1.35$. The ratio of the mean-square displacement to the square of the F to Nd distance is $\langle \Delta X \rangle^2 / R^2 = 5 \times 10^{-3}$, where $R = 2.35 \text{ \AA}$. We estimate the order of magnitude of the isotope shift by comparing V_{ev} as given by the terms in (A1), (A2), and (A3) of the Appendix with the crystalline field due to a single H^- ion. In particular the coefficient of $Y_{4,0}$ due to the x, y, z motions in V_{ev} is the fraction $\langle \Delta X \rangle^2 / R^2 [45/2 - (78/8) \langle \Delta Z \rangle^2 / \langle \Delta X \rangle^2] = 0.05$ times the value of the $Y_{4,0}$ term in a point-charge expansion of the static crystalline field due to a single H^- ion at $R = 2.35 \text{ \AA}$ separation (along X axis from the Nd ion). Rather than compute the point-charge estimate of the latter contribution to the crystalline field, we take as a reasonable and conservative estimate a value of 20 cm^{-1} as compatible with the observed crystalline field splittings. An actual calculation would of course vary somewhat depending on the particular J level. Using the above figures one finds the isotope shift is of the order of $(0.05) (20) (1-2^{-1/2}) = 0.3 \text{ cm}^{-1}$. A similar result obtains from a rough estimate based on Eq. (3), where $\sum \langle \Delta X_i \rangle^2 / r^2 \approx 0.25$, in which r^2 is the mean-square $4f$ radius. Thus one estimates a shift of $(20) (0.25) (1-2^{-1/2}) = 1.5 \text{ cm}^{-1}$. The experimentally found shift is in fact in agreement with these two slightly different estimates, depending on the level.

The actual experimentally observed isotope shift is the difference in isotope shift between the ground and excited states. However, the relative H^- to D^- shift is zero for the 3P_0 of Pr^{3+} and the ${}^2P_{1/2}$ level of Nd^{3+} on account of the vanishing of matrix elements of the form (3). (The remaining first-degree terms of V_{ev} in second-order perturbation contribute a negligible amount.) The observed shifts in these two particular electronic states, therefore, reflect that of the ground level alone (Fig. 4). This shift is to be subtracted from the observed shifts of the other transitions to ascertain the shifts in their excited states. Hence apparent isotope shifts of the order of $+0.6 \text{ cm}^{-1}$ for neodymium and 1.1 cm^{-1} for praseodymium correspond to essentially zero shift for the excited state (within the accuracy of our measurements), as for example ${}^4F_{3/2}$ in NdF_3 . This is consistent with the fact that both Stark components of ${}^4F_{3/2}$ have the same shift.

Figure 4 also shows the energy-level scheme appropriate to the ${}^4F_{7/2}$ level of neodymium in which the isotope shift is negative.

It is worth drawing attention to the fact that the shift of the electronic levels due to the zero-point motion and electron-phonon interaction in hydrogen-

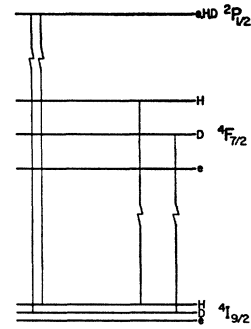


FIG. 4. Transitions to ${}^2P_{1/2}$ and ${}^4F_{7/2}$ in hydrogen-doped and deuterium-doped crystals of NdF_3 showing the nature of the isotope shift. The 0.6 cm^{-1} shift in the ${}^2P_{1/2}$ lines is due to the isotope shift in the ground level. The lines to the lowest crystalline Stark level of ${}^4F_{7/2}$ show a negative isotope shift relative to all the other observed shifts. The levels marked e represent the electronic level in the absence of electron-vibration interaction. The crystalline field and covalency shift are not shown.

doped crystals is negligibly small compared to the shift in the levels due to a changed covalency and crystalline field. Thus the energy-level scheme of Fig. 4 refers to electronic levels in which the shift due to the latter processes are suppressed for clarity.

Imbush *et al.*¹⁹ have found an isotope shift in the R lines of ruby- and chromium-doped MgO which is due to a difference in the amplitudes of zero-point vibration of different isotopes of chromium. Since their crystalline field is larger and mass differences smaller than our case, their isotope shift is smaller but the (unobservable) shift from the position of the line in the absence of zero-point motion is much larger than in our case.

LOCAL MODE VIBRONIC SPECTRUM

The local mode frequencies of both hydrogen and deuterium (Tables I and III) are considerably higher than the LaF_3 lattice frequencies and so as vibronics occur well above the much stronger vibronic spectrum of the pure crystal. It was possible to observe sharp vibronic lines corresponding to local mode frequencies in 6-mm or thicker crystals of hydrogenated and deuterated neodymium fluoride at 4.2°K . Undoped crystals of the same thickness do not show these lines. Table VII gives the vibronic frequencies measured, together with their polarizations, and assignments, where possible, to their parent electronic lines. The remaining unassigned local mode vibronic lines can be used to infer the frequencies of extra electronic lines which are obscured by lines of the pure crystal, and hence cannot be observed directly. These frequencies have already been tabulated in Table VI.

The entire local mode vibronic spectrum consisting of four lines, two of H^- and two of D^- , could not be observed for any single electronic level, as the levels of

¹⁹ G. F. Imbush, W. M. Yen, A. L. Schawlow, G. E. Devlin, and J. P. Remeika, *Phys. Rev.* **136**, A481 (1964).

TABLE VII. Frequency, polarization, and assignment of the local mode vibronics as observed in neodymium fluoride at 4.2°K.

Level Impurity		Vibronic frequency and polarizations (cm ⁻¹)	Parent electronic line (cm ⁻¹)	Separation (cm ⁻¹)	
⁴ F _{3/2}	H ⁻	σ	12462.1±0.1	11580.7	881.3±0.1
		σ	12511.1±0.15	11629.8	881.3±0.15
		σπ	12525.15±0.05
	D ⁻	σ	12213.3±0.15	11581.1	632.2±0.15
		σ	12261.9±0.25	11630.3	631.6±0.25
		σπ	12433.9±0.1	11581.1	852.8±0.1
σπ		12483.6±0.15	11630.3	853.3±0.15	
⁴ F _{5/2}	H ⁻	σπ	13462.4±0.1	12580.7	881.7±0.1
	D ⁻	π ^a	13213.8±0.1	12581.5	632.3±0.1
		π ^b	13230.6±0.1	12598.3 ^b	...
		σπ	13434.5±0.2	12581.5	853.0±0.2
		σπ	13451.3±0.1	12598.3 ^b	...
		σπ	13463.6±0.2	12610.6 ^b	...
⁴ F _{7/2} + ⁴ S _{3/2}	H ⁻	σπ	14380.0±0.1	13497.2	882.8±0.1
		π	14459.8±0.2	13577.0 ^b	...
		σ	14586.0±0.15	13703.2 ^b	...
		σπ	14591.5±0.1	13708.7 ^b	...
		σπ	14690.5±0.2	13497.2	1193.3±0.2
	D ⁻	π	14210.9±0.1	13577.9 ^c ±1	...
		σπ	14343.0±0.5	13710.0 ^c ±1	...
		σπ	14433.4±0.8	13580.4 ^c ±2	...
		σπ	14563.0±0.8	13711.0 ^c ±2	...
		⁴ G _{5/2} + ² G _{7/2}	H ⁻	σ	18137.6±0.1
π	18139.0±0.1			882.6±0.15	
σ	18166.6±0.3			17285.6	881.0±0.3
σ	18220.4±0.3		
σ	18449.7±0.15			17256.5	1193.2±0.2
σ	18534.5±0.3			17341.3 ^b	...
D ⁻	σπ		18109.1±0.1	17257.2	851.9
	σπ		18137.4±0.3	17286.0	851.4
	σπ		18193.6±0.2	17341.7 ^b	...
	σ		18416.5±0.5
	σ	18434.4±0.3	
	σ	18849.5±0.5	
	σπ	18872.0±0.4	

^a Possible presence of σ obscured by broad σ polarized lattice vibronic band.

^b Electronic lines not directly observed, but inferred from the vibronic line using frequency separation found for lowest level of the group.

^c D⁻ electronic lines inferred with the assumption of 632- or 853-cm⁻¹ separation from the D⁻ vibronic.

the next higher electronic multiplet usually occurs low enough to obscure the highest vibronic frequencies.

The vibronics display polarization properties indicative of a high site symmetry for the neodymium ion when partaking in the local mode vibronic absorption process. Although the vibronics of the 1197-cm⁻¹ σ-polarized infrared line are all unpolarized (σπ), those of the 883-cm⁻¹ π-polarized infrared line show σ, π, or σπ polarization depending on the particular electronic level to which it is coupled. Such polarizations cannot be understood in terms of any exact selection rules for any possible site symmetry, but rather must result from approximate selection rules. This situation will now be discussed in some detail.

Thus far we have considered only a single rare-earth

ion interacting with a hydride-ion impurity, although we have presented an argument, based on the infrared selection rules and the infrared data, which requires more than one rare-earth ion to be equidistant from the H⁻ ion for the most abundantly occupied impurity site. In particular we have argued that compatibility with either the bimolecular or hexamolecular x-ray structures (to the extent which is possible) requires distortion of these proposed structures, at least when the H⁻ impurity is present, so that the symmetry is D₃ in the immediate vicinity of H⁻ (see Fig. 1).

It is a simple matter to deduce the vibronic selection rules appropriate to an H⁻ ion bound to three neodymium ions all located in a plane perpendicular to the threefold axis of the crystal with any particular site symmetry for the neodymium ions. We are, however, committed by consistency to consider the neodymium ions as having C₂ symmetry.

Vibronic selection rules, involving a change in only one quantum of vibration for the local mode, can be obtained for a system of an H⁻ surrounded by three equidistant Nd ions by using a product of H⁻ vibrational states and electronic states which in turn are made up of linear combinations of products of three neodymium-ion electronic wave functions, such that the total electronic state belongs to a representation of D₃, but each individual rare-earth-ion wave function is a basis for the local neodymium site group (double group of C₂). The total (vibronic) wave function will belong to a representation of the double group of D₃.

Since the local site symmetry C₂ at each neodymium ion is sufficiently low so as to provide no selection rules by itself, the only selection rules which arise result from the higher symmetry (D₃) of the local grouping of ions. However, in order for such selection rules to be observable there must be energy differences among the various total electronic states which can be formed from electronic states at three neodymium sites. Superexchange would be a possible mechanism for removing the degeneracy, if sufficiently strong.

For example, with each neodymium ion in one of its twofold degenerate ground levels a total of eight states or four energy levels can be formed belonging to 2Γ₆, 2Γ₄, 2Γ₅ of the double group of D₃, Γ₄, and Γ₅ being Kramers conjugate degenerate states. Similarly when one considers one neodymium ion in an excited state, the other two being in their ground state, one finds 8Γ₆ and 4Γ₄, 4Γ₅, or a total of 12 energy levels for the system of three neodymium ions. If all of the four "ground" levels are degenerate with each other and similarly the excited states are also not split, then there is no need to consider such a system of three neodymium ions surrounding an H⁻ ion. All transitions are then allowed in all polarizations.

There is in fact no experimental evidence for such splittings with the resolution used. Each vibronic line involving one quantum of excitation of a local mode appears as a single line.

Thus one must find another way to account for the polarization of some of the vibronic lines. A possible explanation lies in the notion of approximate symmetry. We mean by this, that a particular linear combination of free-ion M states which form a state in the crystal may involve certain M states with relatively large coefficients characteristic of a higher symmetry environment. In other words the lower symmetry terms in the crystalline field are relatively small compared to the higher symmetry terms and the contribution of the former to the intensity would then be relatively small.

Furthermore, it is reasonable in view of our earlier discussion to assume that the effective crystalline potential energy V_c for the rare-earth ion in the presence of H^- replacing an F^- ion is still approximately the same V_c as in the unhydrogenated case for the purpose of calculating energy levels, i.e., for even degree terms. The vibronic selection rules are thus found by examining the following matrix elements:

$$\begin{aligned} (u_2 | z f_z^\alpha | u_1), & \quad \pi \text{ polarization,} \\ (u_2 | x f_x^\alpha | u_1), & \quad \sigma \text{ polarization,} \end{aligned}$$

where u_2 and u_1 are excited and ground electronic wave functions of a single rare-earth ion belonging to irreducible representations of the unhydrogenated rare-earth site group (or approximate group), and the f_i^α are the same as occur in the electronic part of V_{ev} in Eq. (1). In particular, invoking further notions of approximate symmetry discussed above, we assume u_1 and u_2 can be regarded as bases for an approximate site group of even higher symmetry than indicated by resonance experiments, say D_{3h} as in the bimolecular cell model. The f_i^α must then be expanded in terms of functions which are bases for the same approximate site symmetry group (D_{3h} in this example) representations.

As a first approximation one would consider only f_i^α which are of degree one in the coordinates x, y, z , of the $4f$ electron. One obtains the approximate selection rules of Table VIII for such linear terms. It is seen that if a Γ_9 ground state of (approximate) D_{3h} symmetry is the ground state then a vibronic π line can occur to another excited Γ_9 state combined with the local mode appearing at 883 cm^{-1} in π polarization in the infrared. However, when third-degree terms of f_i^α are included then it is found that there are no selection rules and all polarizations are allowed between any two vibronic levels.

Photographic methods do not allow a quantitative determination of the purity of the polarization, especially as the vibronic lines are very weak. The polarization observed could be only approximate and so not be due to any actual high symmetry for the neodymium. This conclusion is likely by the observation that the 883 cm^{-1} localized mode appears in vibronic spectra in $\sigma\pi$, and in σ alone, and π alone, depending on the associated electronic level, which cannot be explained even if *any* other symmetry site were to be assumed.

TABLE VIII. Approximate selection rules for the local mode vibronic transitions for a rare earth with odd number of electrons at a D_{3h} site and involving only terms of degree one in the f electron coordinates in V_{ev} . A applies to the σ -polarized infrared mode at 1197 cm^{-1} and B applies to the π -polarized infrared mode at 883 cm^{-1} .

A			B		
Γ_7	Γ_8	Γ_9	Γ_7	Γ_8	Γ_9
Γ_7	$\pi\sigma$	σ	$\pi\sigma$	σ	σ
Γ_8	σ	$\pi\sigma$	$\sigma\pi$	σ	σ
Γ_9	$\pi\sigma$	$\pi\sigma$	σ	σ	π

It is worth point out for future investigations in other crystals that it is in principle possible to measure the second-degree terms $\langle g \rangle$ of the electron-local mode interaction (1) by making use of the fact that the shift of a vibronic level due to this interaction is different from the shift of a zero-phonon level. Thus by comparing the measured infrared frequency difference $\omega_H - \omega_D$ with the corresponding frequency difference $\omega_H'(\text{vibronic}) - \omega_D'(\text{vibronic})$ as obtained directly from the difference between vibronic and zero-phonon lines we find for the nondegenerate ΔZ mode:

$$\omega_H' - \omega_D' = \omega_H - \omega_D + \langle g_z \rangle (1/M_H \omega_H - 1/M_D \omega_D),$$

where $\langle g_z \rangle$ is the expectation value of the coefficient g_z of the $(\Delta Z)^2$ terms in V_{ev} , Eq. (1) or (A2). A similar expression holds for the ΔX and ΔY degenerate modes except that $\langle g_x + g_y \rangle$ replaces $\langle g_z \rangle$, and one uses the appropriate frequencies ω_H and ω_D .

Clearly to be able to obtain $\langle g_z \rangle$ and $\langle g_x + g_y \rangle$ for a particular electronic level one needs very accurate infrared and vibronic frequencies at the same temperature since the required differences are small.

SUMMARY OF CONCLUSIONS

The H^- ion replaces an F^- ion at a site of D_3 symmetry. The latter symmetry is either a local distortion of a D_{3h} site in the proposed x-ray structures^{6,7} or the F^- ions of the undoped structure already have such locations, which are after all undetectable by x rays. The D_3 site is selectively occupied by H^- doping, although other sites are also occupied to a lesser extent. Only the local modes of hydrogen at the D_3 site appear in vibronic spectra. The substitution of deuterium for hydrogen results in infrared frequencies reduced by a factor 1.4.

The coupling of the localized modes with rare-earth ions is manifested in three ways: (1) as a shift in the electronic levels of the rare-earth ion due to a change in covalency (primarily) and crystalline field (secondarily) for those rare-earth ions which have neighboring F^- ions replaced by H^- ; (2) as an isotope effect for these shifted lines; and (3) as vibronic transitions involving the absorption of a photon by the rare-earth ion accompanied by the creation of one localized phonon.

The isotope effect is found experimentally to depend in magnitude and sign on the electronic level and ranges in value from 0.4 cm^{-1} for the ground level to -2.4 cm^{-1} for ${}^4F_{7/2}$ in NdF_3 . The isotope shift is also found in PrF_3 . The effect is accounted for by the difference in mean square zero-point amplitudes for H^- and D^- acting through the second-degree terms of the electron-phonon interaction in hydrogen-doped and deuterium-doped crystals.

The vibronic transitions are found to involve only those rare-earth ions which have shifted electronic levels due to a neighboring hydrogen. Some vibronic transitions are polarized but the data are not consistent with any point group symmetry site. We can account for the existence of polarized vibronic spectra in NdF_3 only by invoking approximate symmetry and dominant first-degree terms of the crystalline fields. We thus expect the polarizations not to be perfect but only partial under more favorable conditions of observation.

Note added in proof. After the manuscript for the present article was submitted we received an unpublished report by A. Zalkin, D. Templeton, and T. Hopkins, in which a new structure is proposed for LaF_3 based on new x-ray data. The new structure belongs to the space group $D_{3d}^4 (P\bar{3}c1)$. The unit cell of Oftedal⁷ is found to be correct and his La positions accurate, but the F atoms have different positions. In particular, there is now an F site with D_3 symmetry in which the ions are located as we have described in Fig. 1; and these F ions, together with other F ions (not shown) surrounding the La, form a 9-fold coordination of F about La with the latter site having C_2 symmetry. This local arrangement of F ions about La can be recognized as a distortion of D_{3h} symmetry (pointed out by H. Caspers). There are two other F sites in the new structure, one having C_3 , the other C_1 symmetry. The H^- local mode lines A and C of Table I, which by the appearance of the combination $A+C$ arise from the same site, do not fit the selection rules of the C_3 fluorine site. The line E could be due to the H^- at a C_3 site. At present, however, we can say nothing definite about the H^- in sites other than the D_3 site, which is the principal concern of this paper.

ACKNOWLEDGMENT

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APPENDIX

We present explicitly for the point-ion model those second-degree terms of Eq. (1) for the electron-vibration interaction V_{ev} which are needed to give the isotope effect. Only the local modes $Q_i = \Delta X_i$ of the hydrogen ion are included, and for these only squared terms

$$g_x(\Delta X)^2 + g_y(\Delta Y)^2 + g_z(\Delta Z)^2 \quad (\text{A1})$$

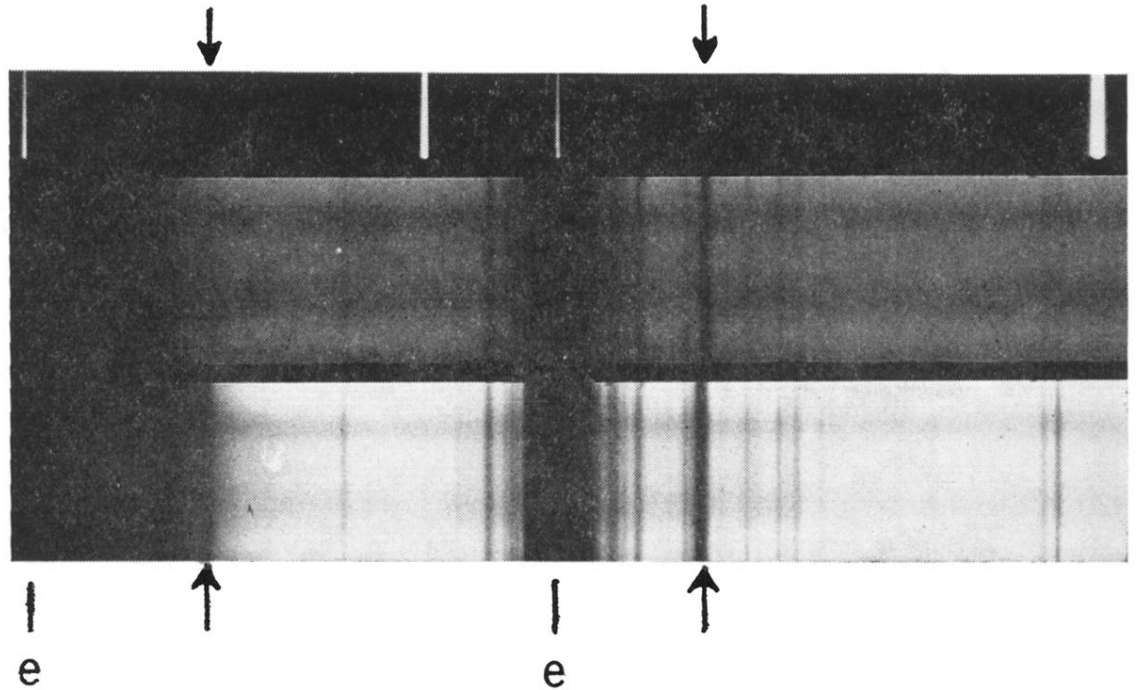
are needed. If the hydrogen ion is located along the Y axis a distance R from a rare-earth ion at the origin, then one obtains

$$g_z = \frac{-e^2}{2R^3} + \frac{3}{4} \left(\frac{\pi}{5}\right)^{1/2} \frac{e^2 r^2}{R^5} \left[6Y_{2,0} + \frac{5}{3}(\sqrt{6})(Y_{2,2} + Y_{2,-2}) \right] \\ - \frac{e^2}{16} \frac{r^4}{R^7} [50Y_{4,0} + 14(\sqrt{10})(Y_{4,2} + Y_{4,-2}) \\ + 3(\sqrt{70})(Y_{4,4} + Y_{4,-4})] + \frac{e^2}{32} \left(\frac{\pi}{13}\right)^{1/2} \frac{r^6}{R^9} \\ \times [490Y_{6,0} + 45(\sqrt{105})(Y_{6,2} + Y_{6,-2}) + 99(\sqrt{14}) \\ \times (Y_{6,4} + Y_{6,-4}) + 13(\sqrt{231})(Y_{6,6} + Y_{6,-6})], \quad (\text{A2})$$

$$g_x \left. \begin{aligned} &= \frac{e^2}{R^3} - 3e^2 \left(\frac{\pi}{5}\right)^{1/2} \frac{r^2}{R^5} [2Y_{2,0} \mp (\sqrt{6})(Y_{2,2} + Y_{2,-2})] \\ &+ \frac{5e^2}{8} (\pi)^{1/2} \frac{r^4}{R^7} [6Y_{4,0} \mp 2(\sqrt{10})(Y_{4,2} + Y_{4,-2}) \\ &+ (\sqrt{70})(Y_{4,4} + Y_{4,-4})] - \frac{7e^2}{4} \left(\frac{\pi}{13}\right)^{1/2} \frac{r^6}{R^9} \\ &\times [10Y_{6,0} \mp (\sqrt{105})(Y_{6,2} + Y_{6,-2}) + 3(\sqrt{14}) \\ &\times (Y_{6,4} + Y_{6,-4}) \mp (\sqrt{231})(Y_{6,6} + Y_{6,-6})], \quad (\text{A3}) \end{aligned} \right\}$$

where the upper sign holds for g_x and the lower sign for g_y .

FIG. 2. Spectrogram showing transitions to ${}^4F_{3/2}$ in NdF_3 at 4.2°K . The upper spectrum shows hydrogen-doped NdF_3 0.25 mm thick, and the lower shows deuterium-doped NdF_3 0.5 mm thick. The lines marked by arrows occur only in the doped crystals, and display the ordinary positive isotope shift, while all other lines are present in both pure and doped crystals. The two strong lines (e) are the normal electronic transitions, and the weak ones are presumably due to imperfections other than hydrogen or deuterium.



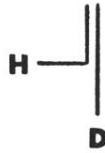
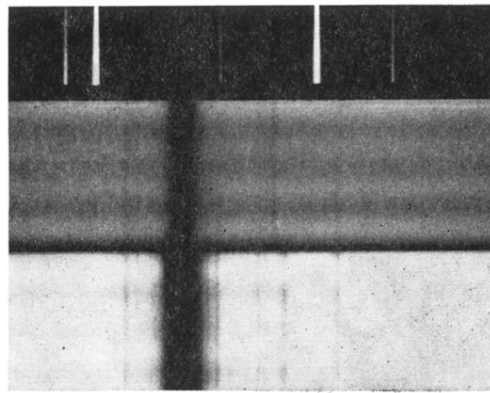


FIG. 3. Spectrogram showing transitions to the lowest crystalline Stark level of ${}^4F_{7/2}$ in NdF_3 at 4.2°K . The upper spectrum shows hydrogen-doped NdF_3 0.25 mm thick, and the lower shows deuterium-doped NdF_3 0.5 mm thick. The lines marked by arrows occur only in the doped crystals and display a negative isotope shift, while all other lines are present in both pure and doped crystals. The strong line is the normal electronic transition, and the weak ones are presumably due to imperfections other than hydrogen or deuterium.