

Lattice Vibrations and Structure of Rare-Earth Fluorides

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The Raman spectra of LaF₃, CeF₃, PrF₃, and NdF₃ have been obtained with an argon-ion laser at room temperature and low temperatures. On the basis of polarizations and intensities of the lines an assignment is made of the Raman-active modes. The infrared-reflectance spectrum was measured with electric vector parallel to the crystal axis. The spectra are consistent with a hexamolecular unit cell, of D_{3d}^4 symmetry, with small distortions from the more symmetrical hexamolecular D_{6h}^3 and bimolecular D_{6h}^4 unit cells proposed earlier. The D_{3d}^4 symmetry appears to offer an explanation of apparent disagreements among earlier studies of these crystals.

INTRODUCTION

THE crystal structure of LaF₃ and its immediate relatives has been the subject of an extensive series of apparently conflicting studies. Knowledge of the crystal symmetry is important to the interpretation of electron-spin spectra, optical-absorption spectra, and other properties, and the lattice vibrations must be understood in order to interpret observed electronic spectra of the solids. We, therefore, undertook the investigation of the Raman spectra of LaF₃, CeF₃, PrF₃, and NdF₃, at room temperature and at 70 or 20°K. The Raman spectrum, with laser excitation, provides a powerful means of examining the crystal symmetry because each component of the polarizability tensor can be measured individually for each vibrational frequency. Both the total number of modes appearing under each polarization and the extent of overlap of bands between different polarizations can give significant information on the symmetry and number of molecules in the unit cell.

The fluorides of La, Ce, Pr, and Nd have the structure of the naturally occurring mineral tysonite, which differs from the normally stable structures of the heavier rare-earth fluorides¹ or the rare-earth chlorides.² A substantial amount of direct experimental evidence has been accumulated concerning the tysonite structure, which cannot be ignored in interpreting new evidence. It was found, in fact, that these earlier studies, though incomplete and apparently contradictory, provide important clues to the true structure and the interpretation of the observed Raman spectrum, as discussed below. A brief review of the earlier work is thus called for at this point. Oftedal³ initially proposed a structure for tysonite with 6 molecules per unit cell and D_6^6 ($P6_322$) symmetry. In a subsequent paper⁴ based on new x-ray results, he raised the symmetry of the hexamolecular cell to D_{6h}^3 ($P6_3$ mcm), and observed that the actual structure deviated only slightly from the "ideal structure," in which a bimolecular pseudocell would become the true unit cell, with symmetry

D_{6h}^4 ($P6_3$ mmc). Van Vleck and Hebb⁵ showed that reported values for the Faraday rotation could be explained by three magnetically nonequivalent La sites, differing by a rotation of the twofold symmetry axis by 120° about the c axis of the crystal, and that the Faraday results were therefore consistent with (but did not prove) Oftedal's D_{6h}^3 structure.

Schlyter⁶ undertook a reinvestigation of the x-ray diffraction spectrum of tysonite and concluded that the true structure was the bimolecular cell with structure D_{6h}^4 discussed by Oftedal. The experimental distinction depended upon weak reflections seen by Oftedal but not observed by Schlyter; the difference in the structures is represented by displacements of the La ions by about 0.05 Å, which is comparable to vibrational amplitudes. In the bimolecular cell the site symmetry of the La ion would be D_{3h} , as compared with C_{2v} in the hexamolecular cell.

Sayre and Freed⁷ found that the absorption spectrum of PrF₃ was consistent with a C_{2v} site symmetry at liquid-nitrogen temperature, but additional lines appeared at liquid-helium temperature that suggested that the positions of minimum energy for certain of the ions were slightly off the planes of vertical symmetry. Electron-spin-resonance measurements by Jones *et al.*,⁸ appeared to confirm the D_{6h}^3 symmetry, but continued study⁹ gave evidence for even lower symmetry than C_{2v} at the La sites. On the other hand, Wong *et al.*¹⁰ found evidence of polarization in the optical-absorption spectrum of praseodymium-doped LaF₃ that required a higher symmetry than C_{2v} , which they suggested could arise from the symmetry of the unit cell (point group D_{6h}) or from a site symmetry of D_{3h} . Krupke and Gruber¹¹ confirmed the polarization measurements and favored a local "distortion" toward D_{3h} symmetry.

New x-ray diffraction studies by Mansmann¹² and by

⁵ J. H. Van Vleck and M. H. Hebb, *Phys. Rev.* **46**, 17 (1934).

⁶ K. Schlyter, *Arkiv Kemi.* **5**, 73 (1953).

⁷ E. V. Sayre and S. Freed, *J. Chem. Phys.* **23**, 2066 (1955).

⁸ D. A. Jones, J. M. Baker, and D. F. D. Pope, *Proc. Phys. Soc. (London)* **74**, 249 (1959).

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

¹⁰ E. Y. Wong, O. M. Stafstudd, and D. R. Johnston, *Phys. Rev.* **131**, 990 (1963); *J. Chem. Phys.* **39**, 786 (1963).

¹¹ W. F. Krupke and J. B. Gruber, *J. Chem. Phys.* **39**, 1024 (1963).

¹² M. Mansmann, *Z. Anorg. Allgem. Chem.* **331**, 98 (1964); *Z. Krist.* **122**, 375 (1965).

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¹ A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.* **75**, 2453 (1953).

² W. H. Zachariasen, *J. Chem. Phys.* **16**, 254 (1948).

³ I. Oftedal, *Z. Physik. Chem.* **5B**, 272 (1929).

⁴ I. Oftedal, *Z. Physik. Chem.* **13B**, 190 (1931).

Zalkin *et al.*¹³ led to the conclusion that the unit cell contained 6 molecules as found by Oftedal, but that the symmetry was lower than D_{6h}^3 and was, in fact, D_{3d}^4 ($P\bar{3}c1$) with C_2 site symmetry of the La. Jones and Satten,¹⁴ studying optical transitions in the rare-earth trifluorides with H^- and D^- impurities, found evidence for a distortion of symmetry about a fluoride ion site from the Oftedal structure. Their results were consistent with the D_{3d}^4 structure. A study of the lattice vibrations by Caspers *et al.*¹⁵ failed to provide conclusive evidence concerning the structure. Goldman and Shen¹⁶ found that spin-spin relaxation in LaF_3 showed two types of fluorine nuclei, present in the ratio of 2/1, as would be expected for the D_{6h}^3 structure but not the D_{6h}^4 bimolecular cell or the hexamolecular D_{3d}^4 structure. Buchanan *et al.*¹⁷ observed no polarization of the Ce^{3+} infrared absorption bands in the LaF_3 lattice, indicating a site symmetry no higher than C_{2v} . The Faraday rotation results are consistent with any of the three proposed structures.

EXPERIMENTAL RESULTS AND INTERPRETATION

Raman spectra were excited with an argon-ion laser and observed with a Spex 1400 tandem spectrometer and a cooled EMI 6256 photomultiplier. Both the 4879.9 and 5145.3 Å lines were employed, with average powers of 100 mW. Slit widths were generally 100 μ , or about 4-cm⁻¹ spectral slit width. Signals were amplified by a Keithley model 610BR electrometer and recorded on a Sanborn 7700 recorder. Time constants were typically 3 to 5 sec.

The plane-polarized laser beam was reflected upward and focused weakly to a point inside the crystal. The scattered radiation was collected along a direction perpendicular to the plane of the laser beam and perpendicular to the crystal axis, to avoid the effects of birefringence associated with the large solid angle of scattered radiation collected,¹⁸ and focused onto the slit of the spectrometer. An analyzing polarizer was placed before the spectrometer slit and a quartz half-wave plate could be added between the laser and the sample to alter the incident plane of polarization. Clear single crystals, about 15 by 7 by 7 mm, oriented with the c axis along the long dimension, were obtained from Optovac. For low-temperature measurements, crystals were cooled by a flow of helium gas at controlled temperature.¹⁹ Lowering of the temperature caused an appreciable sharpening of the bands, thus making it much easier to identify close-lying lines, and also demon-

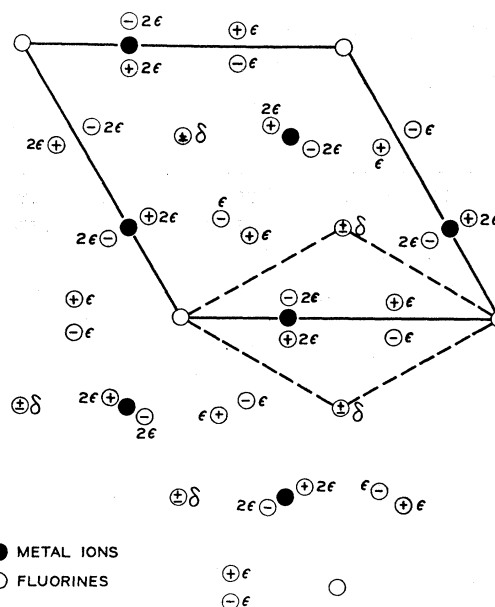


Fig. 1. Unit cell of LaF_3 . The solid line outlines the hexamolecular unit cell, the dashed line the bimolecular cell (or "pseudocell"). The plane shown is $\frac{1}{4}$ lattice unit above the origins of Ref. 20 (pp. 271, 304), for simplicity of representation of position of ions, and the distances of fluorine atoms above or below this plane are indicated. ($\epsilon \approx \frac{1}{3}c$, $\delta \approx \frac{1}{18}c$).

strated that the bands assigned were not second-order bands, which would be expected to decrease strongly in intensity with decreasing temperature.

The Raman spectra are best interpreted by a detailed comparison of the three lattice structures proposed. The projection of ions on to the horizontal plane $z = \frac{1}{4}$ (perpendicular to the z , or c , axis of the crystal) is given in Fig. 1 for the lower half of somewhat more than a single unit cell of the D_{3d}^4 structure.¹³ Designations of lattice sites follow the International Tables.²⁰ The La ions form a triangle at $z = \frac{1}{4}$ and $\frac{1}{2}$ lattice unit from the origin, and another triangle (not shown) at $z = \frac{3}{4}$ rotated by 60° with respect to the first triangle. The 2 a fluorines are at the centers of the triangles $(0, 0, \frac{1}{4})$ and $(0, 0, \frac{3}{4})$ and the 4 d fluorines are on the two other threefold axes, at $\frac{1}{3}, \frac{2}{3}, z$, and $\frac{1}{2} + z$, and at $\frac{2}{3}, \frac{1}{3}, \bar{z}$, and $\frac{1}{2} - z$, with $z = 0.313$. This structure differs from Oftedal's D_{6h}^3 structure in two respects. The 12 g fluorines are displaced from the vertical planes passing through the origin and the La ions by 0.055 lattice units, or 0.423 Å, and the d fluorines are 0.063 lattice units, or 0.463 Å, from the planes of the lanthanums and the a fluorines. The structure shown differs from the bimolecular D_{6h}^4 structure in the same respects (the " d " fluorines should be moved vertically 0.063 units and the " g " fluorines horizontally by 0.055 units), but also because the La ions and the " g " fluorines should be exactly at the points $\frac{1}{3}, 0, \frac{1}{4}$ and $\frac{1}{3}, 0, z$ (and the equivalent points obtained by the C_3 rotation or C_6 screw operation). That is, the least symmetrical of the proposed structures differs from the

¹³ A. Zalkin, D. H. Templeton, and T. E. Hopkins, *Inorg. Chem.* **5**, 1466 (1966).

¹⁴ G. D. Jones and R. A. Satten, *Phys. Rev.* **147**, 566 (1966).

¹⁵ H. H. Caspers, R. A. Buchanan, and H. R. Marlin, *J. Chem. Phys.* **41**, 94 (1964).

¹⁶ M. Goldman and L. Shen, *Phys. Rev.* **144**, 321 (1966).

¹⁷ R. A. Buchanan, H. E. Rast, and H. H. Caspers, *J. Chem. Phys.* **44**, 4063 (1966).

¹⁸ S. P. S. Porto, J. A. Giordmaine, and T. C. Damen, *Phys. Rev.* **147**, 608 (1966).

¹⁹ M. B. Graifman (to be published).

²⁰ *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, England, 1952).

most symmetrical structure proposed by displacement of the four "d" fluorines 0.063 units, displacement of the "g" fluorines by 0.059 units, and displacement of the La ions by 0.0068 units, or 0.049 Å. The bimolecular unit cell is indicated in Fig. 1 by a dotted line.

The selection rules for Raman transitions²¹ are determined by the form of the polarizability tensor relating the initial and final states. Assuming the initial state to be totally symmetric, the polarizability tensor has a symmetry determined by the point group of the unit cell and the irreducible representation to which the lattice mode corresponds. The tensors have the following forms for the point groups D_{6h} and D_{3d} .

D_{6h}

$$A_{1g}: \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_2 \end{pmatrix}, \quad E_{1g}: \begin{pmatrix} 0 & 0 & \alpha_3 \\ 0 & 0 & \alpha_3 \\ \alpha_3 & \alpha_3 & 0 \end{pmatrix},$$

$$E_{2g}: \begin{pmatrix} \alpha_4 & \alpha_5 & 0 \\ \alpha_5 & -\alpha_4 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

D_{3d}

$$A_{1g}: \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_2 \end{pmatrix}, \quad E_g: \begin{pmatrix} \alpha_4 & \alpha_5 & \alpha_3 \\ \alpha_5 & -\alpha_4 & \alpha_3 \\ \alpha_3 & \alpha_3 & 0 \end{pmatrix}.$$

The number of lattice modes corresponding to each irreducible representation is found by reducing the representation for the vibrations. The selection rules (given by the nonzero polarizability tensor components), and the expected numbers of modes, are summarized in Table I. A more detailed description of the symmetry of the vibrations can be found by treating the vibrations of each set of equivalent nuclei separately. The number of nuclei in the set left in place by each symmetry operation is multiplied by the character of a vector displacement and the resultant representation reduced in the standard manner.²² Also, if a set of unit vectors, directed along orthogonal axes, is located on each nucleus, the character of this representation will supply symmetry modes specified in terms of the motions of specific sets of equivalent nuclei along the crystal symmetry axis or perpendicular to it. This additional information is valuable in attempting to correlate observed transitions with the individual normal modes of the lattice. Of course, the actual normal modes will be linear combinations of all the symmetry modes transforming under the same irreducible representation. Mixing will be especially important for symmetry modes expected to have similar frequencies.

The magnitudes of the displacements that differentiate the three symmetries are sufficiently small (but not negligible) compared to vibrational displacements that one can readily predict certain consequences. If the

²¹ S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (Andhra University, Waltair, India, 1951), 2nd ed.

²² See Ref. 21, pp. 74-77, or R. P. Bauman, *Absorption Spectroscopy* (John Wiley & Sons, Inc., New York, 1962), pp. 462-465 and 450, or E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955).

TABLE I. Expected numbers of optical modes.

Point Group Molecules/unit cell	D_{6h}^4 2	D_{6h}^3 6	D_{3d}^4 6
Raman-active			
$A_{1g}(\alpha_{xx} + \alpha_{yy}; \alpha_{zz})$	1	3	5
$E_{1g}(\alpha_{xz}, \alpha_{yz})$	1	4	12
$E_{2g}(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$	3	8	
Infrared-active ^a			
$A_{2u}(M_z)$	2	4	6
$E_{1u}(M_x, M_y)$	2	7	11

^a A_{2u} and B_{2u} (inactive) of D_{6h} combine to form A_{2u} of D_{3d} ; similarly, E_{1u} and E_{2u} (inactive) combine to form E_u .

atoms were in the most symmetrical structure, certain of the integrals appearing in the transition probabilities would be exactly zero because of symmetry. When the ions are displaced, these integrals will no longer be exactly zero, but for small perturbations the effects on the integrals will be small and the transition probabilities will be small. Further displacements will have similar effects, increasing intensities of certain previously forbidden lines. In principle, therefore, assuming the structure found by Mansmann and Zalkin *et al.*, one might expect to observe certain strong lines characteristic of the bimolecular structure, some less intense lines forbidden for the bimolecular unit cell but allowed for the D_{6h}^3 structure, and some weaker lines allowed only for the D_{3d}^4 structure. Also, lines allowed in a given polarization only for low symmetry may be substantially weaker than the same lines in a polarization for which they are "fully allowed."

Examination of the spectra in the light of these expectations shows a remarkable degree of correspondence. The observed spectrum of LaF_3 is shown in Fig. 2, obtained with 5145 Å excitation at 70°K. The experimental polarization conditions are specified by the notations²³ of the form $x(zx)y$, in which the first letter indicates the axis of the crystal along which the beam is incident, the second and third letters (in parentheses) give the plane of the electric vector of the incident and scattered radiation, respectively, and the final letter indicates the crystal axis along which the scattered radiation is observed. (In these crystals the z axis is taken as the symmetry axis of the crystal and the x and y axes are equivalent.)

For the structure of highest symmetry, one band is expected in the $x(zz)y$ spectrum and one band in the $z(xz)y$ spectrum, both attributable to fluorine motions. One very strong band is observed in each spectrum (Figs. 2a and 2d), both at high frequencies (390 and 290 cm^{-1}). Three bands would be allowed for the $z(yx)y$ orientation, one arising from motions of the lanthanum ions and two from motions of the fluorines. Very strong bands are observed at 79, 366, and 315 cm^{-1} , the first easily identified with the lanthanum motion and the others with fluorine modes. The spectrum obtained with $z(xx)y$ orientation shows the strong bands observed in $x(zz)y$ and $z(yx)y$ orientations, but not those of the

²³ T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.* 142, 570 (1966).

TABLE II. Assignment of Raman-active lattice modes of LaF₃, CeF₃, PrF₃ and NdF₃.

Symmetry species	Selection rules	D_{6h}^4 modes	Observed bands ^a	Additional D_{6h}^3 modes	Observed bands ^a	Additional D_{3d}^4 modes	Observed bands ^a
A_{1g}	$\left\{ \begin{array}{l} \alpha_{xx} + \alpha_{yy} \\ \alpha_{zz} \end{array} \right\}$	(g)F (z)	$\left\{ \begin{array}{l} 390 \\ 396 \\ 401 \\ 414 \end{array} \right\}$	$\left\{ \begin{array}{l} M(x) \\ (g)F(x) \end{array} \right\}$	$\left\{ \begin{array}{l} 120 \\ 120 \\ 125 \\ 128 \\ 305 \\ 310 \\ 315 \\ 322 \end{array} \right\}$	$\left\{ \begin{array}{l} (g)F(x) \\ (d)F(z) \end{array} \right\}$	$\left\{ \begin{array}{l} 231 \\ 237 \\ 237 \\ 247 \\ 283 \\ (?) \\ 302(?) \\ 310(?) \end{array} \right\}$
E_{1g}	$\left\{ \begin{array}{l} \alpha_{xz} \\ \alpha_{yz} \end{array} \right\}$	(g)F (x)	$\left\{ \begin{array}{l} 290 \\ 305^b \\ 301 \\ 319 \end{array} \right\}$	$\left\{ \begin{array}{l} M(z) \\ (g)F(z) \\ (g)F(x) \end{array} \right\}$	$\left\{ \begin{array}{l} 145 \\ 141 \\ 145 \\ 143 \\ 226 \\ 232 \\ 245 \\ (?) \\ 203 \\ (?) \\ 206 \\ 210 \end{array} \right\}$		
E_{2g}	$\left\{ \begin{array}{l} \alpha_{xx} - \alpha_{yy} \\ \alpha_{xy} \end{array} \right\}$	$\left\{ \begin{array}{l} M(x) \\ (g)F(x) \\ (a+d)F(x) \end{array} \right\}$	$\left\{ \begin{array}{l} 79 \\ 78 \\ 79 \\ 81 \\ 366 \\ 388 \\ 370 \\ 391 \\ 315 \\ 318 \\ 321 \\ 328 \end{array} \right\}$	$\left\{ \begin{array}{l} M(x) \\ (a)F(x) \\ (d)F(x) \\ (g)F(x) \\ (g)F(z) \end{array} \right\}$	$\left\{ \begin{array}{l} 145 \\ 138 \\ 145 \\ 150 \\ 325 \\ (?) \\ (?) \\ (?) \\ 301 \\ (?) \\ \approx 306 \\ (?) \\ 281? \\ \approx 282? \\ (?) \\ (?) \\ 163 \\ (?) \\ 166 \\ 170 \end{array} \right\}$		

^a The four bracketed values are wave numbers (in cm⁻¹) for LaF₃, CeF₃, PrF₃, and NdF₃, reading top to bottom. Fluorine modes under E_{2g} are probably strongly mixed and therefore not separately identifiable. Letters (a, d, g) preceding the F (for fluorine) indicate lattice sites, as given in Ref. (20) for D_{3d}^4 , while the (x) or (z) following M or F indicate motions primarily perpendicular or parallel to the "c" axis. M stands for La, Ce, Pr or Nd.

^b Room-temperature value.

$z(xz)y$ spectrum, in accordance with the D_{6h} selection rules.

If the symmetry were precisely that of the D_{6h}^3 point group, all those vibrations found for D_{6h}^4 symmetry would be expected but in addition there should be two modes of symmetry A_{1g} , three of symmetry E_{1g} , and five of symmetry E_{2g} , with one of each symmetry attributable to a lanthanum motion and the remainder to fluorine motions. Two moderately strong bands are found in the $x(zz)y$ spectrum, at 120 and 305 cm⁻¹. Of these, the 120-cm⁻¹ band, which is quite certainly a lanthanum motion, is absent in all other orientations and the 305-cm⁻¹ band appears also in $z(xx)y$ but not in the other orientations shown. Two bands are found in the $z(xz)y$ spectrum, at 145 and 203 cm⁻¹, with a probable third fundamental lattice mode at 226 cm⁻¹. Five bands are expected in the $z(yx)y$ spectrum [and these should appear also in $z(xx)y$, along with the two bands allowed for $x(zz)y$]; bands are found at 145, 325, 301, 282, and 163 cm⁻¹.

Under the D_{3d}^4 symmetry, no additional bands would be expected for the degenerate representations, E_{1g} and E_{2g} , although these will be merged into a single species E_g so that all modes allowed under $z(xz)y$ should also be permitted under $z(yx)y$ and $z(xx)y$ and all modes allowed under $z(yx)y$ and therefore allowed also under $z(xx)y$ should be permitted to appear under the $z(xz)y$ polarization conditions. There is little evidence of such overlapping (primarily bands at 315, 203, and 145 cm⁻¹), presumably because the asymmetry from D_{6h} is sufficiently small that the "cross talk" will be very weak. There should, however, be two additional bands allowed in the $x(zz)y$ and $z(xx)y$ orientations. These are identifiable as the band at 231 and, probably, the band at 283 cm⁻¹, both corresponding to fluorine motions. The assignments are summarized in Table II, in which the four bracketed numbers represent the observed wave numbers in LaF₃, CeF₃, PrF₃, and NdF₃, reading from top to bottom. The modes are labeled by the symmetry modes expected, in which M represents the

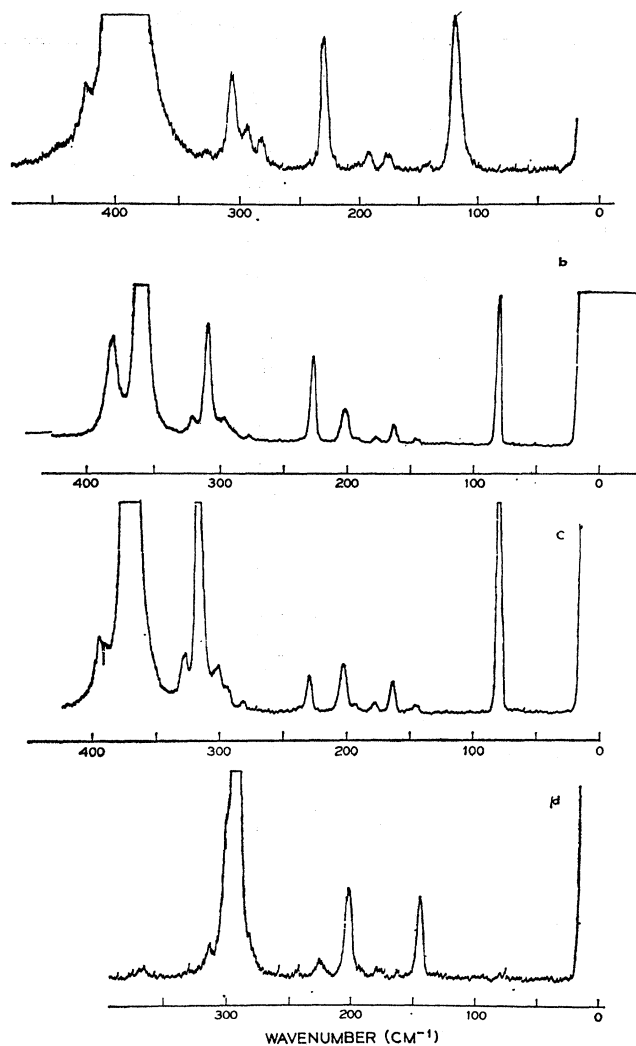


FIG. 2. Raman spectra of LaF_3 at 70°K . Orientation conditions are: $a: x(zz)y$, $b: z(xx)y$, $c: z(yx)y$, $d: z(xz)y$. Wave-number displacements from the $\lambda 145\text{-}\text{\AA}$ exciting line are shown in cm^{-1} .

metal (La, Ce, Pr, or Nd), F the fluorines with prefixes identifying the positions of the fluorines in the D_{3d^4} structure, and the "z" or "x" in parentheses indicates that the mode is parallel to the crystal axis or in the plane perpendicular to the axis. Because of approximate accidental degeneracies, several of the weaker bands are lost in the shoulders of stronger bands but their positions can be surmized by comparison with the other crystals. The low-temperature values are listed. These generally differ by a few cm^{-1} from room-temperature wave numbers.

In addition to the bands discussed, some very weak bands are observed that can be attributed to "leakage" due to small crystal misalignments or to second-order bands. For example, in the $x(zz)y$ spectrum shown there is some evidence of the 290, 203, and 145 cm^{-1} E_g bands. The very weak bands at 177 and 192 cm^{-1} , which do not fit selection rules and apparently have no detectable analogs in the spectra of the other crystals, may be second-order bands. The apparent sharp bands at approximately 412 cm^{-1} and 395 cm^{-1} , in Figs. 2a and 2c, respectively, are instrumental in origin and do not ap-

pear in other spectra obtained under similar conditions.

The spectrum of PrF_3 (xx component) is shown for comparison purposes in Fig. 3. The strong resemblance to the LaF_3 spectrum is at once apparent. The additional bands evident at 66, 94, and 537 cm^{-1} arise from the low-lying electronic levels of the praseodymium ion. This electronic Raman effect is under continuing study and will be reported elsewhere.

The infrared-reflectance spectrum, from 500 to 113 cm^{-1} , was measured at room temperature with the electric vector parallel to the crystal axis. Thus only bands of symmetry A_{2u} were observed. Four bands were found, as shown in Fig. 4. It is likely that two additional bands would be apparent in absorption measurements but are substantially weaker than those detected. From the behavior of the three strongest bands one may estimate the positions of the longitudinal modes to be about 379, 226, and 172 cm^{-1} , with the corresponding transverse modes at about 324, 196, and 162 cm^{-1} . The weaker band is centered at about 281 cm^{-1} . The absence of any good correlation between these infrared-active bands and the Raman bands is expected for any of the models discussed, since all have a center of symmetry.

FIG. 3. Raman spectrum (xx) component of PrF_3 at 20°K. Wavenumber shifts, from the 5145-Å exciting line, are shown in cm^{-1} . Some electronic Raman bands are evident. (See text.)

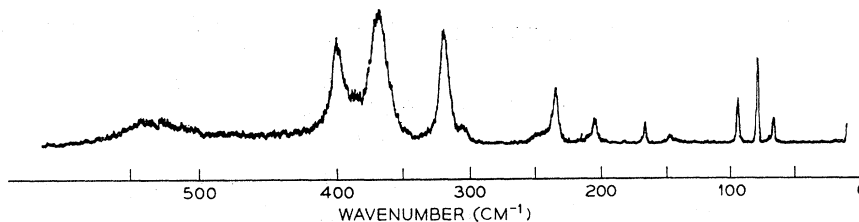
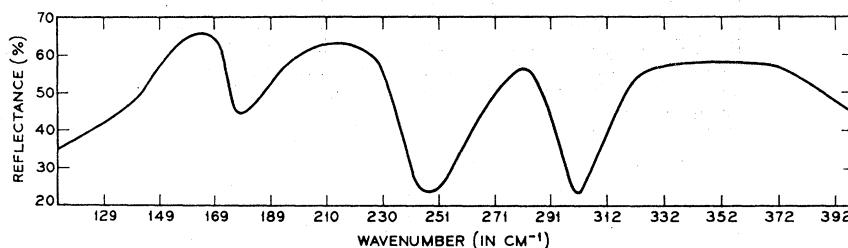


Fig. 4. Infrared reflectance of LaF_3 , with electric vector parallel to crystal axis.



DISCUSSION

By analogy with the spectra of molecules, one may describe the intensity of a Raman transition as a consequence of two properties, the "bond polarizability" and the symmetry. The first determines the intensity for a fully allowed transition and will differ, in general, for different types of motions. The symmetry determines whether the effects of the individual motions add or subtract. In the Raman spectra of the rare-earth fluorides we are observing primarily the differences attributable to different symmetries. In certain other experiments, such as optical absorption or electron spin resonance, the effects and the general importance of local symmetry may be substantially different. For example, the four fluorines on d sites and the two fluorines on a sites are equivalent in the bimolecular D_{6h}^4 cell, but different from the 12 fluorines on "g" sites ("f" sites in D_{6h}^4 notation). The small perturbation of these fluorines does not substantially destroy the equivalence of the "a" and "d" sites for purposes of spin-spin relaxation measurements, though these 6 fluorines are easily distinguished from the 12 fluorines at the "g" sites.

The Raman spectra observed provide convincing evidence that the symmetry of these rare-earth fluorides is D_{3d}^4 , as reported by Mansmann and by Zalkin *et al.*, and also that the deviations of the symmetry from the more symmetrical models discussed by Oftedal and by Schlyter are indeed small. Thus it is not surprising that in the many different types of measurements that have been reported for these crystals the small asymmetries are sometimes quite apparent and are at other times undetected.

The arguments in support of D_{3d}^4 symmetry from our Raman measurements may be summarized as follows:

- Five totally symmetric (A_{1g}) bands are found, even at low temperature. Only three are expected for D_{6h}^3 and one for D_{6h}^4 .
- Twelve degenerate bands are observed, as expected for D_{3d}^4 or D_{6h}^3 (whereas only four are expected for D_{6h}^4). Of these, three appear in orientations corre-

sponding to more than one symmetry species of D_{6h} . This is forbidden for any structure of D_{6h} symmetry but is permissible under D_{3d} selection rules.

The arguments in favor of the distortions from the D_{6h}^4 and D_{6h}^3 structures being small are the following:

- The intensity relationships show that only the one A_{1g} , the one E_{1g} , and the three E_{2g} bands expected for D_{6h}^4 are especially strong.
- The failure to observe 75% of the degenerate bands in the alternate orientation (α_{xx} and α_{yy} as against $\alpha_{xx} - \alpha_{yy}$ and α_{xy}) indicates that the symmetries of the vibrational wave functions are lowered only slightly from that of the D_{6h}^3 structure.
- The appearance of four infrared-reflectance bands polarized parallel to the unique axis, of which the two at 196–226 and 324–379 seem significantly stronger than the two at 162–172 and about 281 cm^{-1} , is consistent with moderate distortion from D_{6h}^4 and only slight distortion from D_{6h}^3 symmetry (which should allow an additional two bands to appear beyond those observed).

Furthermore, it appears that only such a model involving small distortions from a structure of higher symmetry would be capable of explaining the diversity of prior experimental results in the literature. While this argument is less relevant to interpretation of the Raman spectra, it cannot be ignored so long as we assume the structures studied by all workers were in reality the same.

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