[16]R. E. Peierls, Phys. Rev. 54, 918 (1938).

[17]L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1959).

[18]For other values of the spin quantum number one cannot obtain the entropy as an explicit function of m and x. Analogous problems for any value of the spin can nevertheless be easily solved by expressing the entropy as a function of two Lagrange multipliers related to m and x. See, for instance, A. Castets, thèse de 3^c cycle (Paris, 1972) (unpublished); and A. Castets and M. Nauciel-Bloch, Solid State Commun. (to be published).

[19]"Quadrupolar" ordering always occurs as a first-order transition as a consequence of Landau's theory of symmetry changes associated with phase transitions. Indeed, the "quadrupolar" ordering corresponds to an order parameter belonging to the D_2 irreducible representation of the group O(3) of all rotations around a fixed point, and the symmetrical cube of D_2 contains the identical representation [cf. N. Boccara, Ann. Phys. (N.Y.) (to be published).] There is no such requirement for the ferromagnetic ordering, which can be (and is) found to be either first or second order.

[20]H. H. Chen and P. M. Levy, Phys. Rev. Letters 27, 1383 (1971). In this letter a nonmagnetically ordered phase is predicted at zero temperature for isotropic and Ising-like spin-one systems with large biquadratic exchange.

PHYSICAL REVIEW B VOLUME 5, NUMBER 11 1 JUNE 1972

Far-Infrared Stark and Zeeman Splitting of Pr^{3+}, Nd^{3+}, Er^{3+}, Ho^{3+}, and Dy^{3+} in Some Lanthanide Fluorides

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The Zeeman effect has been studied in several rare-earth ions imbedded in lanthanide fluorides. A special cryostat has been constructed with two liquid-helium tanks. One, at 4 K, contains a superconducting coil giving magnetic fields as high as 60 kOe. The other, at 1.3 K, contains a Ge:Ga bolometer to detect far-infrared radiation. Large splittings, as high as 30 cm^{-1}, have been observed with Nd^{3+}, Er^{3+}, and Dy^{3+} where the ground state is a Kramers doublet. For Pr^{3+} and Ho^{3+}, which do not give Kramers doublets, the effect of a magnetic field is not so significant. The effect is negligible for Pr^{3+}. For Ho^{3+}, a 3-cm^{-1} shift and a line broadening are observed. On the other hand, whereas the spectra of $LaF_3:Nd^{3+}$ and NdF_3 are very similar, for PrF_3 a pair of ions seems to be present and gives twice as many electronic lines compared to $LaF_3:Pr^{3+}$. Localized modes are observed close to 73 cm^{-1} for both Er^{3+} and Dy^{3+}, while an absorption band is observed at 64 cm^{-1} for Dy^{3+} which seems to be slightly sensitive to the magnetic field and has still to be explained. An average spectroscopic g value for the ground-state and first-excited-state Kramers doublet has been calculated for Nd^{3+}, ER^{3+}, and Dy^{3+}. For the ground-state Kramers doublet, these values are well within the limits of the reported g tensor based upon ESR. For the first-excited-state Kramers doublet the determinations are, respectively, $g_2 = 1.7$, 3.6, and 11.5 and they constitute new data.

I. INTRODUCTION

The electric field in a crystal at a rare-earth-ion site may split the ground state to produce a series of sublevels extending from zero to a few hundred wave numbers in energy. Transitions between these sublevels may be infrared active, and a number of them have been observed at temperatures low enough to get rid of the absorption occurring from two-phonon difference modes.[1] Lanthanum fluoride is a good host for rare-earth ions because it can be grown in large-size crystals which are not hygroscopic.

A few studies in the far infrared have been published and a lot of low-frequency lines have been described.[2-5] Nevertheless, all the absorption lines are not due to electronic transitions, as we thought in our first paper.[2] The spectra are certainly complicated by low-frequency infrared-active phonon modes. Fortunately, in the case of lanthanum fluoride the phonon spectrum is simple enough to make it possible to identify the pure lattice absorption unambiguously by looking at the whole series of lanthanide fluorides.

Only relatively small frequency shifts are expected from compound to compound because the increase in the rare-earth-ion mass is small from lanthanum to erbium: La = 139, Ce = 140, Pr = 141, Nd = 144, Dy = 163, Ho = 163, and Er = 168.

The increase in mass seems largely compensated by an increase of force constants due to the increase in ionic size.

The remaining absorption lines are not necessarily all due to electronic excitations. In the case

of a doped crystal, they may arise from local modes characteristic of the doping impurity, or they may reveal the whole phonon spectrum with peaks corresponding more or less accurately to maxima in the density of modes in the phonon spectrum of the host crystal. The use of a magnetic field which is efficient only on light-mass electrons is then needed to distinguish electronic transitions which can be shifted or split by the Zeeman effect from lattice excitations which are insensitive. Very high magnetic fields are necessary to modify the electronic transitions of paramagnetic ions where the magnetic-dipole moment is relatively small.

Magnetic fields as high as 50 000 to 100 000 Oe are needed, and for a long time they were at the disposal of only a few laboratories. The use of superconducting coils has now brought these facilities to most physicists. However, a special cryostat has to be used with a light pipe leading the far-infrared radiation to the core of the coil where the sample is placed.

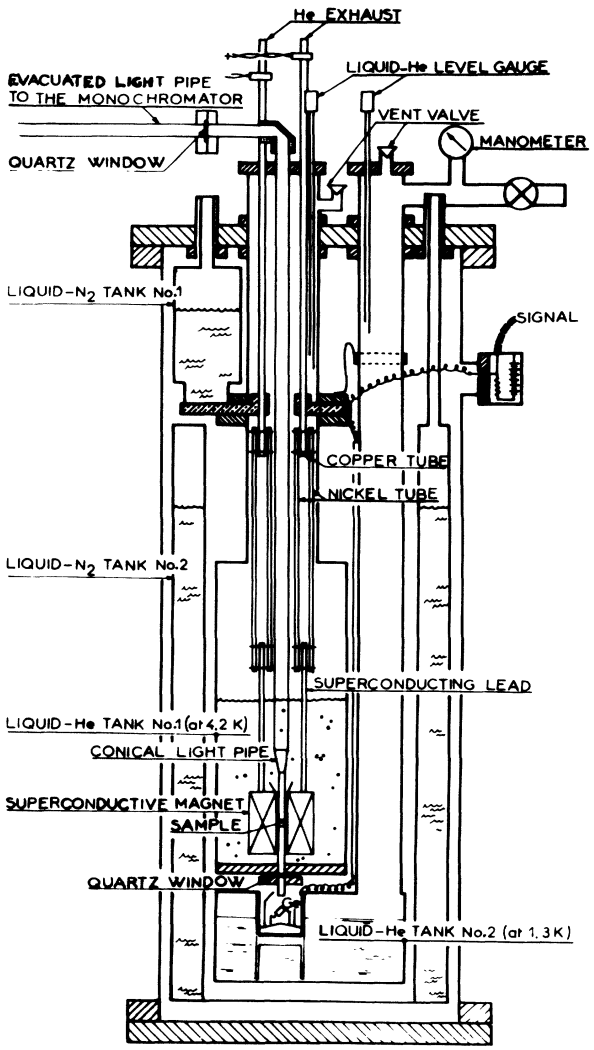

FIG. 1. Cryostat for the study of Zeeman effect in the far infrared.

This technique is very flexible but leads to important losses of radiation and the most sensitive detector of radiation has to be used. For the past few years this detector has been a bolometer made of a germanium generally doped with gallium with a sensitivity which is two or three orders of magnitude larger than the Golay cell. This detector works at 1 K, while the superconducting coil is used at 4 K and two helium tanks are necessary for the cryostat.

Now we must not forget that all these low-lying electronic levels have energy corresponding to those of the continuum of lattice vibration frequencies. We can expect interaction of the electronic states with the nearby phonon modes. This could be detected by the breadth of the electronic lines or by a modification of some characteristic phonon lines when the magnetic field brings an electronic line close to its frequency. There are vague indications of such interactions in a few papers (Ref. 3, p. 134; Ref. 6, p. 482; Ref. 7, p. 3275).

II. EXPERIMENTAL

The crystals are from Optovac. They are shaped into cylinders perpendicular to the c_3 axis of the crystal. The cylinder is mounted in a light pipe ($\phi = 7$ mm) coaxial with the magnetic coil (Fig. 1). The radiation entering the light pipe comes from a far-infrared grating monochromator.[8] The complete light pipe is separated from the monochromator by a quartz window. The other end of it holds the sample in the center of the superconducting coil and is partly filled with liquid helium. The upper vertical part of the light pipe can be removed for changing the sample. The operation takes 20 min and requires 0.1 liter of liquid helium. The small lower part under the sample cannot be removed.

The germanium bolometer is one of the best and has been described elsewhere.[9] It is located in a cavity communicating with the vacuum surrounding liquid-helium tank No. 1.

The radiation enters this cavity by a light pipe $\phi = 7$ mm mechanically independent of the upper one to avoid any distortion due to a different expansion of liquid-helium tanks No. 1 and No. 2. Figure 2 gives a closer view of the germanium bolometer. The insulated copper lead to the germanium bolometer is imbedded in an indium plate in contact with the liquid-helium tank to get rid of any important heat transport from the cryostat wall to the bolometer, which has to work at the lowest possible temperature permitted by the cryostat (about 1.3 K).

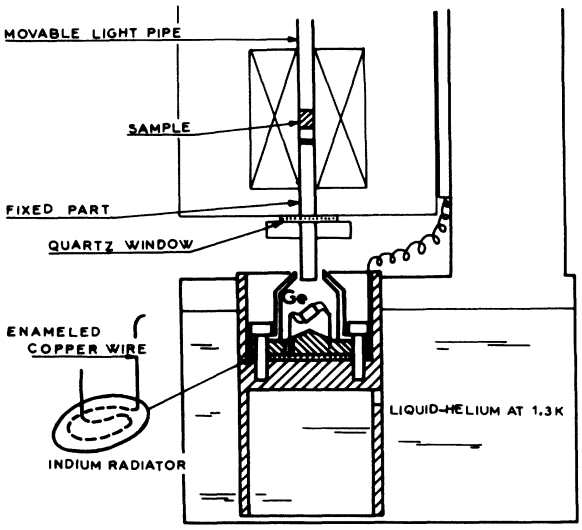

FIG. 2. Close view of the germanium bolometer.

III. INFRARED-ACTIVE LATTICE MODES

In Fig. 3 we can see the absorption spectrum of pure lanthanum fluoride for the three possible orientations of the crystal with respect to the polarized incident beam. The 27.5-cm^{-1} line is found mainly in the π spectrum and arises from an electric-dipole transition parallel to the c_3 axis. It shifts to 25 cm^{-1} when the temperature is increased from 25 to 80 K. The 100–108- and 127-cm^{-1} lines are found in the σ spectrum and ought to appear in the axial spectrum if they represent electric-dipole transitions perpendicular to the c_3 axis.

All four lines are found in the different lanthanide fluorides and might be explained in terms of one phonon absorption at point Γ, though the 27.5-cm^{-1} frequency gives a small absorption which disappears at room temperature,[4] probably because of temperature broadening. Figure 4 gives the absorption spectrum of cerium fluoride: The 100- and 108-cm^{-1} lines are mixed into one band but the sample is not oriented.

IV. ELECTRONIC TRANSITIONS IN Nd^{3+}

A. Lattice Vibrations or Pure NdF_3

The absorption spectra of pure NdF_3 in zero magnetic field have been described for axial, π, and σ polarizations.[4]

The lattice line at 34 cm^{-1} for $T = 18$ K is sensitive to temperature as most lattice lines are, and is found at 32 cm^{-1} for $T = 80$ K. It appears only in the π spectrum and is assigned to an electric-dipole transition parallel to the c_3 axis. The 106-cm^{-1} absorption band of the σ spectrum corresponds to the 100–108-cm^{-1} lines of LaF_3, which are no longer separated in NdF_3 (as in the case of CeF_3). It is found at 104 cm^{-1} in the axial spectrum (the shift is not significant because of the linewidth), and appears slightly at 109 cm^{-1} in the π spectrum, probably because of the convergence of the beam on the sample. The band shifts to a lower frequency when the temperature is increased up to 80 K.

B. 45-cm^{-1} Band in Pure NdF_3

In the same way, the 45.5–44.5- and 43.5-cm^{-1} bands observed in spectra a, π, and σ, respectively, in pure NdF_3 cannot be considered as significantly

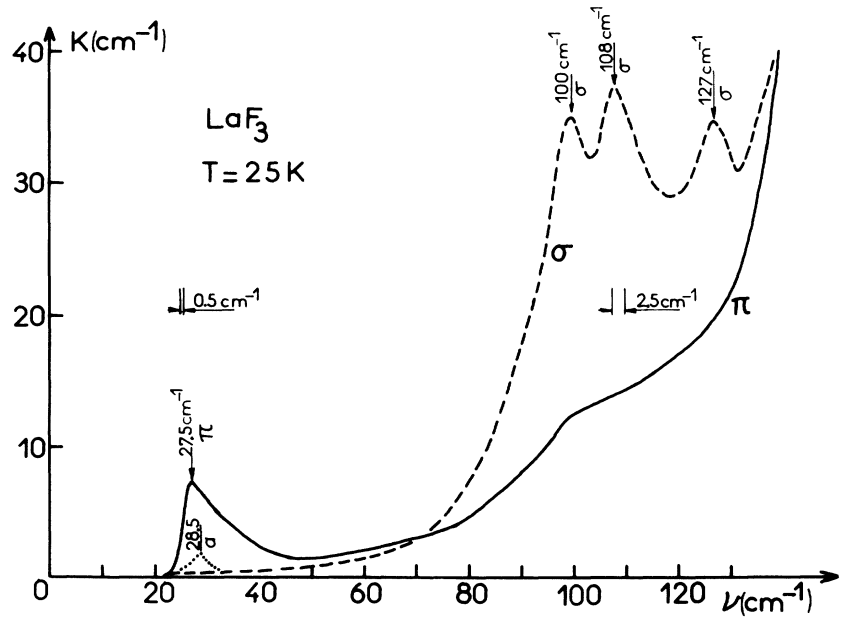

FIG. 3. Absorption coefficient of IaF_3 at 25 K from 20 to 120 cm^{-1} for π and σ orientations. The data are obtained from samples 1–7 mm thick.

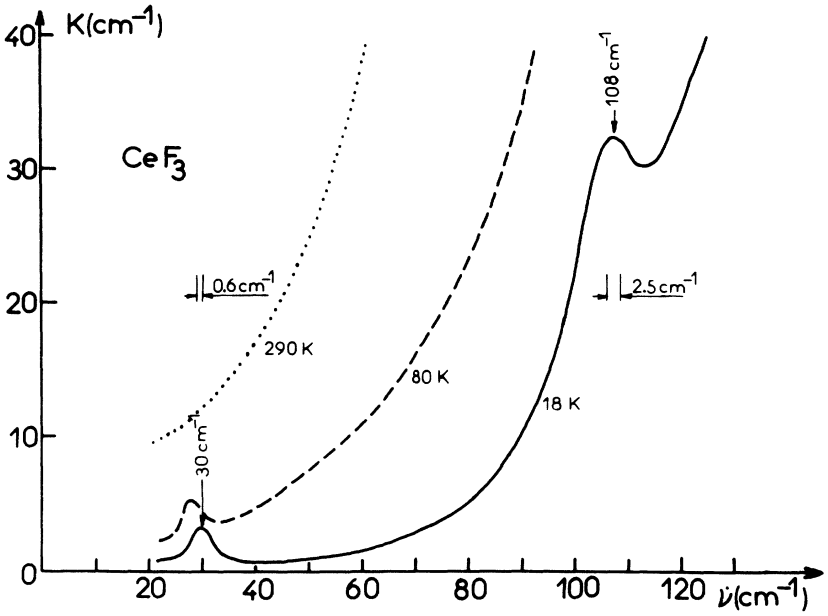

FIG. 4. Absorption coefficient of CeF_3 at different temperatures (unoriented sample).

different. The frequency does not depend upon temperature, and the intensity vanishes at room temperature. They represent one electric, nonpolarized transition.[3,4] Figure 5 shows effectively that the line is linearly displaced by the magnetic field.

C. 45-cm^{-1} Band in LaF_3: Nd^{3+}

Figure 6 shows the same transition in LaF_3: Nd^{3+} in zero magnetic field (full curve). The absorption curve shows some asymmetry with a half-intensity width (about 2.7 cm^{-1}) smaller than in pure NdF_3 (about 4 cm^{-1}), but the frequency remains unchanged and is a good check of previous computations of the Stark splitting of the ground state $^4I_{9/2}$ of the Nd^{3+} ions in LaF_3.[10]

Five Kramers doublets labeled Z_1–Z_5 have been calculated.[10] The three lowest are represented in the center of Fig. 7. When a magnetic field is applied, the linewidth is increased up to 7 cm^{-1} and its center is shifted to 47 cm^{-1} for 30 kOe, as in the case of pure NdF_3 for the same field. However, for 50 kOe, the two components are now clearly separated at 45.5 and 49.5 cm^{-1}.

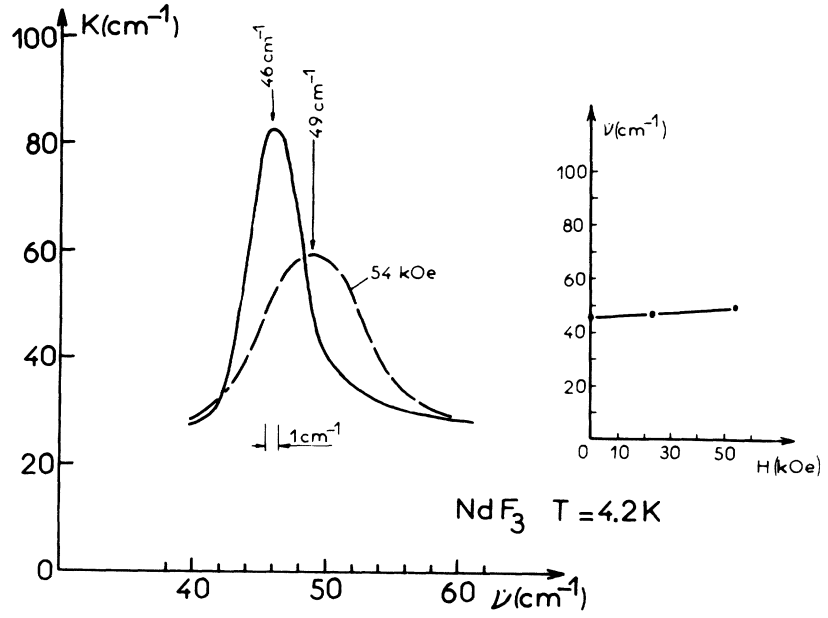

FIG. 5. Absorption coefficient of NdF_3 at 4.2 K around 46 cm^{-1} for a 54-kOe magnetic field applied perpendicular to the crystal axis. The data are obtained from a 0.2-mm-thick sample.

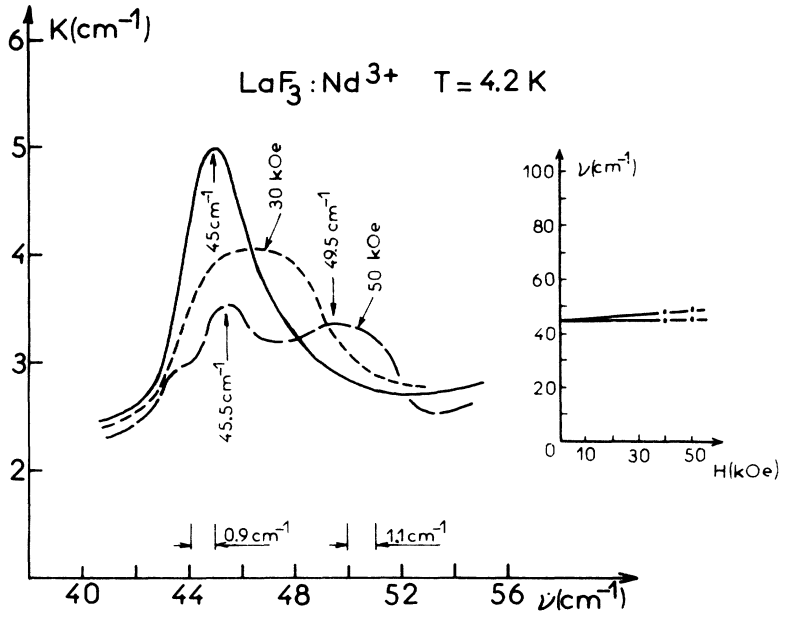

FIG. 6. Absorption coefficient of $LaF_3 : Nd^{3+}$ at 4.2 K for different magnetic fields applied perpendicular to the crystal axis. The absorption band is split into a doublet whose components are shifted linearly with the magnetic field intensity. The data are obtained from a 4-mm-thick sample.

If the ions were completely unquenched, we should use the free-ion Landé g factor given by $g_J = \frac{3}{2} + [S(S+1) - (L+1)]/2J(J+1)$. However, even if J is a good quantum number, and because of the crystal-field splitting of some of the $2J+1$ different M_J states, the effective g governing the splitting may be very different from g_J and may be highly anisotropic.[11]

For the ground-state Kramers doublet we have

$$E_1 = -\tfrac{1}{2} g_1 \mu_B H ,$$

$$E_2 = +\tfrac{1}{2} g_1 \mu_B H .$$

For the next doublet we have

$$E_3 = 45\ \text{cm}^{-1} - \tfrac{1}{2} g_2 \mu_B H ,$$

$$E_4 = 45\ \text{cm}^{-1} + \tfrac{1}{2} g_2 \mu_B H .$$

$\mu_B = 0.47 \times 10^{-4}\ \text{cm}^{-1}\text{Oe}^{-1}$ is the Bohr magneton. Hence $\mu_B H = 2.35\ \text{cm}^{-1}$ for $H = 5 \times 10^4$ Oe; g is the effective spectroscopic Zeeman factor for the ion in the crystal.[12] Hence we have

$$\nu_1 = E_3 - E_1 = 45\ \text{cm}^{-1} + \tfrac{1}{2}\mu_B H(g_1 - g_2) = 45.5\ \text{cm}^{-1} ,$$

$$\nu_2 = E_4 - E_1 = 45\ \text{cm}^{-1} + \tfrac{1}{2}\mu_B H(g_1 + g_2) = 49.5\ \text{cm}^{-1} ;$$

then $g_1 = 2.13$ and $g_2 = 1.70$.

Now two weaker lines ν_3 and ν_4 arising from the E_2 level are expected:

$$\nu_3 = 45 - 4.5 = 40.5\ \text{cm}^{-1} ,$$

$$\nu_4 = 45 - 0.5 = 44.5\ \text{cm}^{-1} .$$

The ν_4 frequency might explain the inflexion near 44 cm^{-1}; the ν_3 is beyond the range of the study.

Our g_1 value is very different from the free-ion g_J factor in the ground state ($g_J = \frac{8}{11}$). It is not in contradiction with the electron-spin-resonance (ESR) determinations[12] for the ground state: $g_z = 3.11$, $g_x = 1.356$, $g_y = 1.092$, $\Theta = 45°$ being the angle between the c_3 axis of the crystal and the z axis which is the principal direction of the g tensor corresponding to the largest principal g_z value. Our g values are close to those made previously by far-infrared techniques[13] where the applied magnetic field is also approximately perpendicular to the crystal axis: $g_1 = 2.1 \pm 0.2$ and $g_2 \simeq 1.4 \pm 0.1$. In fact, Parrish's measurements are impeded by

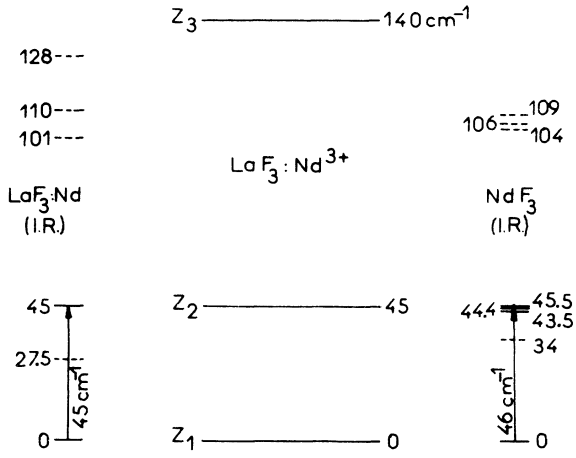

FIG. 7. Lower-energy states of Nd^{3+} in LaF_3 calculated by Caspers in the center (Ref. 10) and from our measurements (left side). The right side corresponds to pure NdF_3.

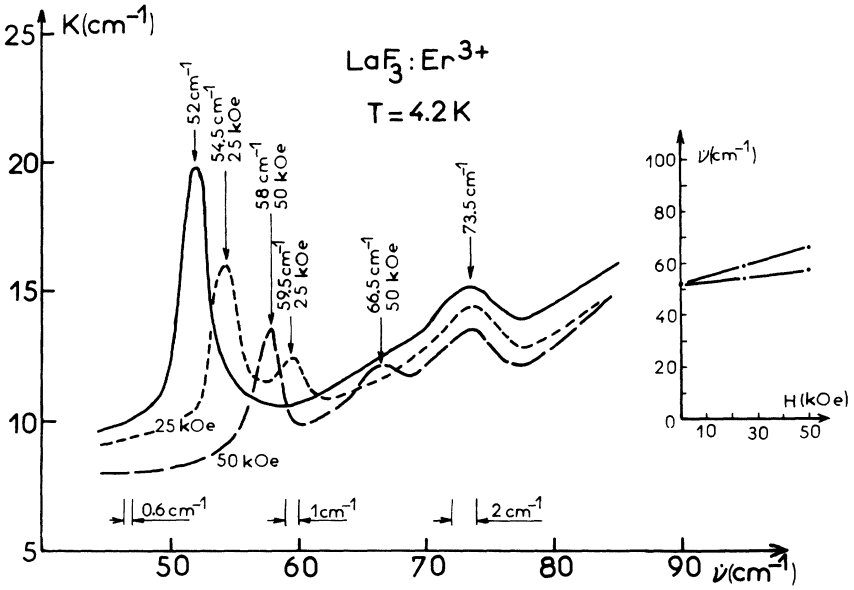

FIG. 8. Absorption coefficient of $LaF_3:Er^{3+}$ at 4.2 K. The absorption band is split into a doublet whose components are linearly shifted by the magnetic field applied to the crystal. The crystal axis is perpendicular to the field (the data are obtained from a 1-mm-thick plate).

a weak lattice line observed at 51 cm^{-1} in zero magnetic field whose intensity decreases as the magnetic field is applied. This is an argument for the authors to suggest "vibronic coupling" with the electronic transition. We did not see any evidence of this impurity lattice absorption in spite of the very close experimental conditions (except that we used a superconducting coil instead of a Bitter magnet).

V. ELECTRONIC TRANSITIONS IN Er^{3+} AND Dy^{3+}

In both cases $J = \frac{15}{2}$ in the ground state, which

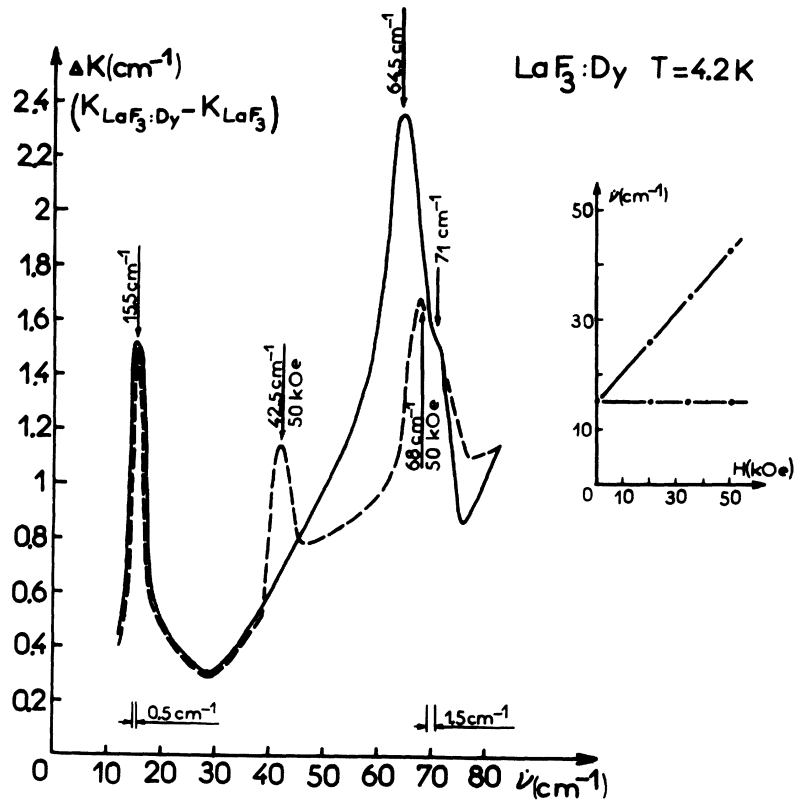

FIG. 9. Absorption coefficient ΔK of Dy^{3+} in LaF_3 at 4.2 K. The absorption band at 15.5 cm^{-1} is split into a doublet. The 15.5-cm^{-1} component is insensitive to the increase of the magnetic field; the other component is linearly shifted up to 42.5 cm^{-1} for a 50-kOe intensity. The data are obtained from a 6-mm-thick sample.

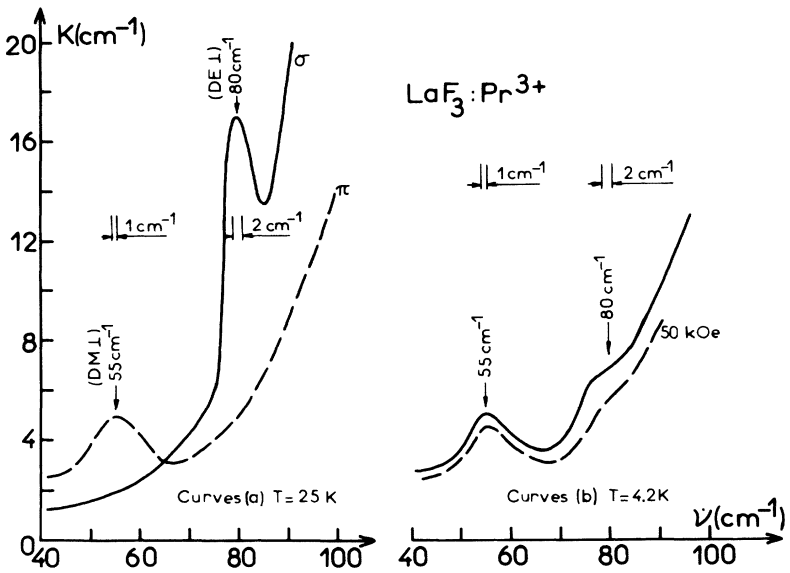

FIG. 10. Absorption coefficient of $LaF_3:Pr^{3+}$. The (a) curves give the σ and π spectra obtained with a sample thickness ranging from 1.5 to 7 mm. The (b) curves show the effect of a 50-kOe magnetic field applied perpendicular to the crystal axis. They are obtained with a 5.5-mm-thick sample. The radiations are nonpolarized.

thus is split into eight Kramers doublets by the LaF_3 crystal field. In zero magnetic field two or three lines are found between the pure lattice absorption bands. They are located at 52 and 73.5 cm^{-1} for $LaF_3:Er^{3+}$ (Fig. 8) and at 15.5, 64.5, and 73.4 cm^{-1} for $LaF_3:Dy^{3+}$ (Fig. 9).

The action of a magnetic field splits both of the first lines at 52 and 15.5 cm^{-1}, which are thus assigned to electronic transitions. It does not affect significantly the last two at 73.5 and 73.4 cm^{-1}, which are thus ascribed to local modes, though the Er^{3+} ion has a larger mass (168) than the Dy^{3+} ion (163). This increase of mass is largely compensated by an increase of the force constant because of a larger ionic radius and a decrease of the lattice parameters. On the other hand, the absorption band of Dy^{3+} at 64.5 cm^{-1} shows definitely a decrease of intensity when the magnetic field pushed the highest-frequency component of the electronic doublet towards its frequency. There is also a slight increase of frequency. In the case of Er^{3+}, a slight decrease of the local-mode intensity at 73.5 cm^{-1} is also observed.

Now we shall look separately at each electronic transition.

A. Electronic Line of Er^{3+} at 52 cm^{-1}

We shall suppose that at 4 K both lines ν_1 and ν_2 of the observed doublet are issued from the lower E_1 level. Hence we have

$$\nu_1 = E_3 - E_1, \quad 58 = 52 + (\tfrac{1}{2}g_1 - \tfrac{1}{2}g_2)\,\mu_B H\,,$$

$$\nu_2 = E_4 - E_1, \quad 66.5 = 52 + (\tfrac{1}{2}g_1 + \tfrac{1}{2}g_2)\,\mu_B H\,.$$

Thus $g_1 = 8.8$ and $g_2 = 3.6$. Now from ESR[3] for the ground state, $g_Z = 10.89$, $g_X = 2.99$, and $g_Y = 4.91$, $\Theta = 45°$ being the angle between the z axis and the c_3 axis of the crystal.

In a different far infrared work,[5] where the applied magnetic field made an angle of 45° with respect to the optic axis of the crystal (90° in our study), the Zeeman effect was said to lead to six components instead of the two that we observed. This was explained in terms of three magnetically distinguishable erbium substitutional sites in LaF_3. There is definitely not any absorption line at frequencies lower than 55 cm^{-1} in our 50-kOe spectrum, while they described three Zeeman-component frequencies ranging from 50 to 55 cm^{-1}. They

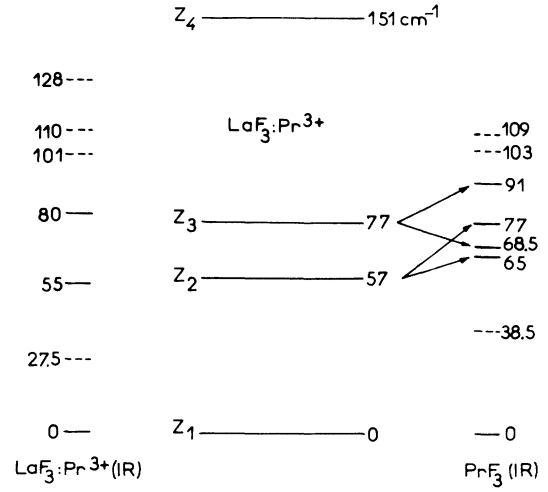

FIG. 11. Lower energy levels of $LaF_3:Pr^{3+}$ as they have been observed (left side) and as they have been calculated by Caspers (center). The right side shows the energy levels that we have observed for pure PrF_3.

were led to g values ranging from 7.5 to 1.5.

B. Electronic Lines in Dy^{3+} at 15.5 cm^{-1}

Let us assume the same scheme for Dy^{3+} as for Er^{3+}. We have

$$\nu_1 = 15.5 = 15.5 + \tfrac{1}{2}(g_1 - g_2)\,\mu_B H\ ,$$

$$\nu_2 = 42.5 = 15.5 + \tfrac{1}{2}(g_1 + g_2)\,\mu_B H\ .$$

Hence $g_1 = g_2 = 11.5$. Now from ESR[12] for the ground state, $g_z = 13.8$, $g_x = 7$, $g_y = 1.5$, and $\Theta = 9°$.

VI. ELECTRONIC TRANSITIONS IN Pr^{3+}

Figure 10 (on the left side) gives the σ and π spectra of $LaF_3 : Pr^{3+}$ showing two lines at 55 cm^{-1} (π) and 80 cm^{-1} (σ) which could pretty well fit the $Z_1 - Z_2$ and $Z_1 - Z_3$ transitions indicated in the center of Fig. 11, where the energies of the levels have been taken from spectroscopic measurement in the visible region.[4] Nevertheless, we see in Fig. 10 (on the right side) that the action of a 50-kOe magnetic field is negligible. We must recall that there are no Kramers doublets in the case of Pr^{3+} where $J = 4$, with a ground state $^3H_4$ which is split completely into nine sublevels in the low-symmetry (C_{2v}) crystalline field of the LaF_3 host at the site of the ion. The Zeeman effect is a second-order effect[13] and appears to be negligible in this experiment.

In the case of pure PrF_3 four lines have been described[2] between the lattice absorption bands at 38 and 91 cm^{-1}, as can be seen in Fig. 11 (right side). Here again no shift is observed under the action of a magnetic field (Fig. 12), except a narrowing of the 65-cm^{-1} absorption band. Nevertheless, the 69- and 77-cm^{-1} lines occur predominantly in the π spectrum as the 55-cm^{-1} line found in $LaF_3 : Pr^{3+}$, while the 91- and 68-cm^{-1} lines are mostly in the σ spectrum as the 80-cm^{-1} line of $LaF_3 : Pr^{3+}$. Hence the possibility of an explanation in terms of a coupling between two praseodymium ions, splitting the 80-cm^{-1} σ line into the 91- and 68-cm^{-1} components ($D_{E\perp}$) and splitting the 55-cm^{-1} π line into the 65- and 77-cm^{-1} components ($D_{M\perp}$).

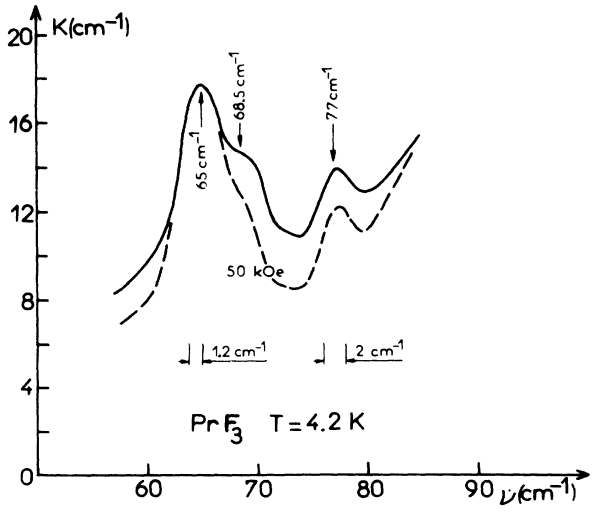

FIG. 12. Absorption coefficient of pure PrF_3 at 4.2 K with and without a magnetic field applied perpendicular to the crystal axis. The data are obtained from a 1.3-mm-thick sample.

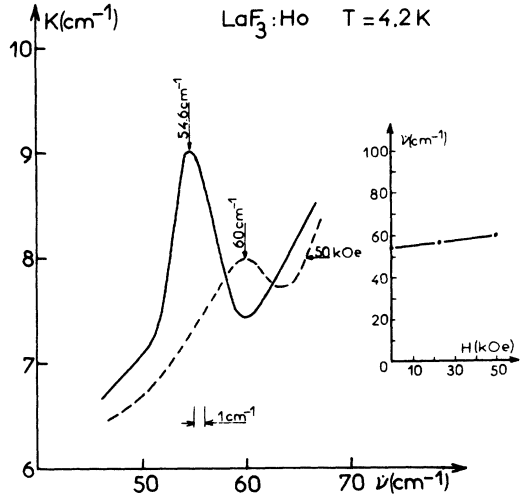

FIG. 13. Absorption coefficient of $LaF_3 : Ho^{3+}$. The absorption band at 54.6 cm^{-1} is shifted to 60 cm^{-3} when a 50-kOe magnetic field is applied perpendicular to the c_3 axis. The linewidth is increased from 4 to about 10 cm^{-1}. The data are obtained from a 3-mm-thick sample.

Let us recall that all four components are found in the axial spectrum and have been classified as perpendicular electric-dipole ($D_{E\perp}$) and perpendicular magnetic-dipole ($D_{M\perp}$) transitions, as is pointed out above. The 55-cm^{-1} absorption band of $LaF_3 : Pr^{3+}$ should be $D_{M\perp}$, and the 80-cm^{-1} band should be $D_{E\perp}$. The same characters are observed for the band of pure $PrCl_3$ at 31 and 100 cm^{-1}, and no splitting is observed which could be an indication of coupling between pairs of ions in that case.

VII. ELECTRONIC TRANSITION IN Ho^{3+}

In Ho^{3+} there are ten $4f$ electrons and the ground state $^5I_8$ will be split into seventeen Stark levels by the crystal field in LaF_3; only one far-infrared absorption band is observed in $LaF_3 : Ho^{3+}$ besides the lattice absorption. It is located at 54.6 cm^{-1}, with a 4-cm^{-1} width (Fig. 13). While $LaF_3 : Pr^{3+}$ was not significantly sensitive to a magnetic field, here we observe a shift towards higher frequencies, a decrease of peak intensity, and a broadening of the band. We can assume that we observe either the unresolved splitting of a first excited Stark level or the shift of a single first excited Stark level.

In the second assumption the broadening should

occur from different possible sites of the Ho^{3+} ion which might have different g values, hence from several components which should not be separated.

VIII. CONCLUSION

The study of a series of lanthanum fluorides either pure or doped has enabled us to describe four lattice vibrations which are located at 27.5 cm^{-1} (π component) and 100–108 and 127 cm^{-1} (σ component) for LaF_3 at 25 K. Specific electronic transitions have been demonstrated in Nd^{3+}, Er^{3+}, Dy^{3+}, and Ho^{3+} by the effect of a magnetic field with dramatic shifts as high as 30 cm^{-1} for 50 kOe in the case of Dy^{3+}. However, the light-pipe geometry precluded any precise Zeeman study with polarized radiation. Moreover, there are six ions in the unit cell with identical but differently oriented g tensors. They are derived from one another by 120° rotation about the crystal axis and reflection in the plane perpendicular to it.[12] Each of the six lanthanide sites will have a slightly different Zeeman splitting. Consequently, only an average spectroscopic g value for the six lanthanide sites could be determined in our experiments where the magnetic field is located in a direction perpendicular to the c_3 axis of the crystal. For the ground Kramers doublet these g_1 values are 2.13, 8.8, and 11.5 for Nd^{3+}, Er^{3+}, and Dy^{3+}, respectively, which is well within the limits of the reported g tensor based upon the electron spin resonance.[12–15] For the first-excited-state Kramers doublet the g_2 values are 1.7, 3.6, and 11.5 and could not be determined from ESR.

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