Finally, we note that the present results serve for finding *gyroelectrics* and *hypergyroelectrics* among known ferroelectrics. The gyroelectrics and the hypergyroelectrics are[23,3] those crystals whose gyration (or optical rotatory power) and *electrogyration*, respectively, are nonzero at zero electric field and reversible in sign by means of an electric field; here electrogyration is defined[23,3] as the rate of change of the gyration with the electric field at zero value of the electric field. The gyroelectric and hypergyroelectric crystals must be

ferroelectric. Which of the actual ferroelectrics should be gyroelectric, which hypergyroelectric, and which neither gyroelectric nor hypergyroelectric can readily be found by comparing Table I in the present paper with Tables IV and V in Ref. 3. (Since SbSI is not very transparent, it is unsuitable for use as a gyroelectric.)

ACKNOWLEDGMENT

[23] K. Aizu, Phys. Rev. **133**, A1584 (1964).

Far-Infrared Electronic Transitions in Ions and Pairs of Ions

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In ruby (1% Cr_2O_3), we found two dichroic lines at 100 and 270 μ; in pure praseodymium chloride, two dichroic lines at 100 and 325 μ; in diluted samarium chloride (5%Sa^{3+} in $LaCl_3$), two lines at 100 and 250 μ. A tentative explanation is given for all these lines as transitions between sublevels of the ground-state split either by the crystalline field or by exchange forces between neighboring ions.

I. INTRODUCTION

FOR a few years, we have known that all crystals become as completely transparent in the far infrared at liquid-helium temperature[1] as they generally are in the visible at room temperature. So it is possible to search for electronic transitions of ions imbedded in various lattices. Of course they are low-frequency transitions. The very close levels which take part may be the different components of the ground level of an ion slightly split by the crystal field (as the case with the $4f$ states of rare-earth ions, where the $4f$ electrons are generally considered as well shielded from the crystal field). However, there are other splitting possibilities, for instance slight coupling between two neighbor ions. This paper will show that both types of transitions lead to absorption lines whose intensity is far from negligible.
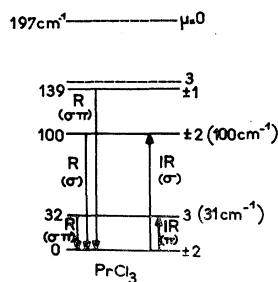

Fig. 1. Stark splitting of the $^3H_4$ ground state of Pr^{3+} in pure $PrCl_3$.

[1] A. Hadni, J. Claudel, E. Decamps, X. Gerbaux, and P. Strimer, Compt. Rend. **255**, 1595 (1962).

II. RARE-EARTH IONS

1. Anhydrous Praseodymium Chloride

The praseodymium ion has two $4f$ electrons and the total angular momentum is $J=4$. (In a magnetic field, each J state is split into $2J+1$ sublevels characterized by the quantum number M_J.) In pure praseodymium chloride, each Pr^{3+} ion is in an electric field of C_{3h} symmetry and the 9 components will include 3 Kramers doublets. Their symmetry is given either by the classical notation $A'A''E''E'$ or the Hellwege's quantum crystal numbers $\mu=0, 3, \pm1, \pm2$, respectively. The selection rules for electric-dipole transitions are

	A' $\mu=0$	E'' $\mu=\pm1$	E' $\mu=\pm2$	A'' $\mu=3$
A' $(\mu=0)$	$\cdots$	$\cdots$	σ	π
E'' $(\mu=\pm1)$	$\cdots$	σ	π	σ
E' $(\mu=\pm2)$	σ	π	σ	$\cdots$
A'' $(\mu=3)$	π	σ	$\cdots$	$\cdots$.

All but two sublevels (in dotted lines), are given on Fig. 1 by the spectroscopy, in the visible, of doped lanthanum chloride single crystals at liquid-helium temperature. All these levels, and another one at 197 cm^{-1} [tentatively interpreted as the A' $(\mu=0)$ missing one], have given electronic Raman lines in a sample of pure praseodymium chloride.[2]

[2] J. T. Hougen and S. Singh, Phys. Rev. Letters **10**, 406 (1963).

The far-infrared spectra are given on Figs. 2–4. The line at 100 μ is a σ one; the line at 325 μ is a π one. In Fig. 4 we see both lines in the axial spectrum of a second plate cut perpendicular to the axis.

In conclusion, we can say that both lines originate from transitions between levels indicated on Fig. 1. The line at 100 cm^{-1} is allowed by the selection rules
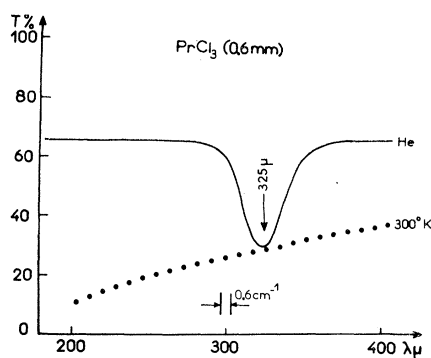

FIG. 2. Transmission of a plate ($e=0.6$ mm) of PrCl$_3$, axis horizontal, unpolarized radiations ($\pi+\sigma$ spectrum).

concerning electric dipole transitions and has the right polarization. The 31-cm^{-1} line is forbidden and probably comes from a magnetic-dipole transition. The maximum value of the absorption coefficient, at 31 cm^{-1}, is $k_M \simeq 7$ cm^{-1}. The intensities of the magnetic-dipole transitions are proportional to those of the electronic Raman lines, and Hougen and Singh have seen that all
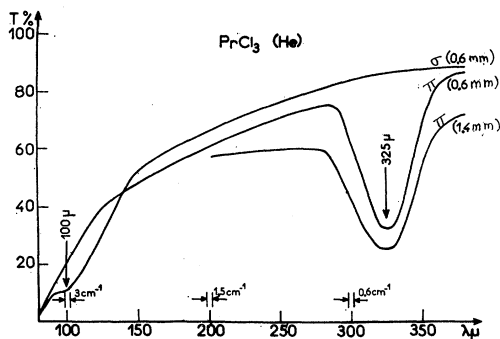

FIG. 3. Transmission of two plates of PrCl$_3$ ($e=0.6$ mm and $e=1.4$ mm), axis horizontal, polarized radiations: σ spectrum and π spectrum.

Raman lines between the lowest Stark level of the $^3H_4$ state of the ion and the other ones are strong—even stronger, sometimes, than the vibrational Raman lines of the lattice.

2. Diluted Anhydrous Samarium Chloride (5% Sa^{3+} in LaCl$_3$)

The samarium ion possesses five $4f$ electrons and the total angular momentum is $J=\frac{5}{2}$. (In a magnetic field,
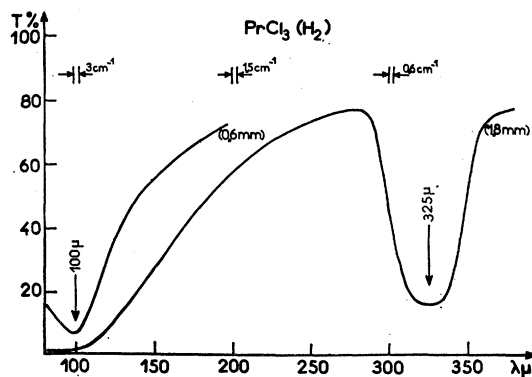

FIG. 4. Transmission of a plate of PrCl$_3$ ($e=1.8$ mm and $e=0.6$ mm), cut perpendicular to the axis, unpolarized radiations: axial spectrum.

the Zeeman effect would split each state into 6 levels labeled by the quantum number M_J: $M_J=\pm\frac{5}{2}$, $\pm\frac{3}{2}$, $\pm\frac{1}{2}$.) In the crystal the electric field has the symmetry C_{3h} and two levels with opposite M_J are not separated: The ground state is split into 3 Kramers doublets whose
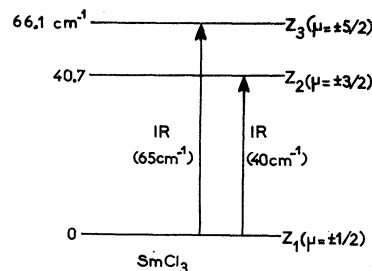

FIG. 5. Stark splitting of the $^6H_{5/2}$ state of the Sa^{3+} ion in LaCl$_3$.

positions are known from absorption and fluorescence spectra,[3] Fig. 5.

Two lines are observed in the far infrared at liquid-helium temperature at 40 and 65.5 cm^{-1} (Fig. 6). Their positions agree perfectly well with the scheme of Fig. 5.
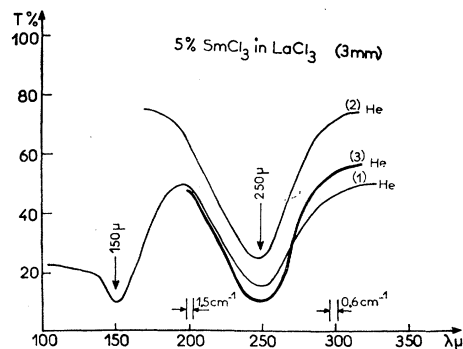

FIG. 6. Transmission of a single crystal of LaCl$_3$ doped with Sa (5%). The plate is very roughly parallel to the axis. Curve 1: unpolarized radiations. Curves 2 and 3, polarized radiations, E horizontal: (2)=axis horizontal; (1) and (3)=axis vertical.

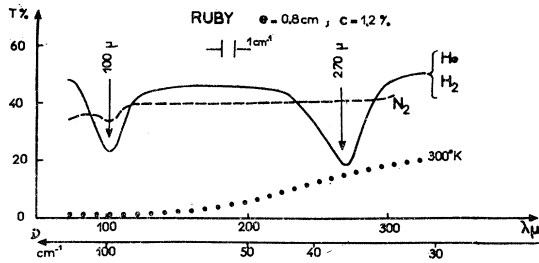[3] M. S. Magno and G. H. Dieke, J. Chem. Phys. **37**, 2354 (1962).

FIG. 7. Axial spectrum (unpolarized radiations, wave vector parallel to the optical axis).

FIG. 10. The 4 levels of a pair of Cr^{3+} ions in the ground state, for an antiferromagnetic coupling.

The orientation of the crystal was probably insufficiently precise and we did not find any polarization effect. If we take into account both the dilution and the general lattice absorption, the maximum k_M of the absorption coefficient would be $k_M \simeq 45$ cm^{-1} at 250 μ.

We remark that both lines are somewhat wider than the pure-praseodymium ones. In spite of what is expected,[2] the absorption lines in a diluted crystal are not always sharper than in a pure one.
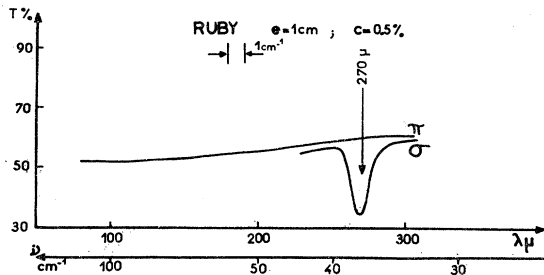

FIG. 8. π spectrum: wave and H vectors, both perpendicular to the optical axis; and σ spectrum: wave and E vectors, both perpendicular to the optical axis.

III. CONCENTRATED RUBY (-1% CHROMIUM IONS)

In Fig. 7 (axial spectrum), we see two lines. Both of them persist at liquid-hydrogen and disappear at liquid-nitrogen temperature (with some restrictions for the line at 100 μ, which is still visible, though much fainter), and at room temperature the broad lattice absorption is considerable. With polarized radiation (Fig. 8), the σ spectrum is identical to the axial one
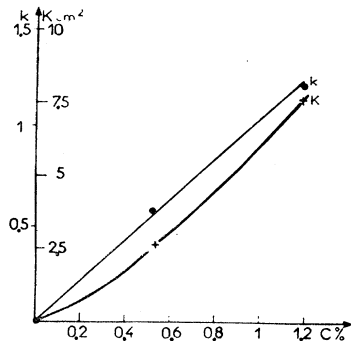

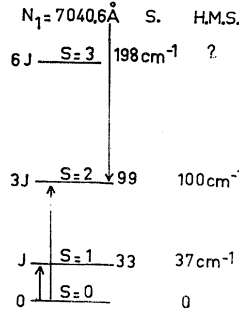FIG. 9. Variations of k and $K = \int k_\nu d\nu$ for $\lambda = 270 \mu$, versus chromium concentration.

and the π spectrum does not exhibit any line.[4] We can conclude that both are electric dipole transitions, with the change of the electric moment perpendicular to the optical axis, ($k_M \simeq 2$ cm^{-1} at 270 μ, for a 1% concentration in chromium ions).

The variations of the absorption coefficient k and of $K = \int k_\nu d\nu$ with chromium concentration show that, for both lines, the chromium ions are responsible for the
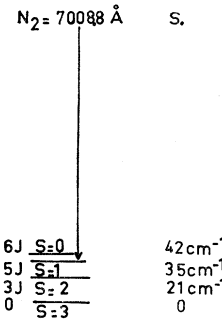

FIG. 11. The 4 levels of a pair of Cr^{3+} ions in the ground state, for a ferromagnetic coupling.

absorption (Fig. 9), but it is nearly impossible to say if the law is a linear or a parabolic one, because of the inhomogeneity of the most concentrated rubies at our disposal.

Absorption and fluorescence spectra in the red have led Kisliuk, Schawlow, and Sturge[5] to the schemes of Figs. 10 and 11. They give the sublevels of the ground
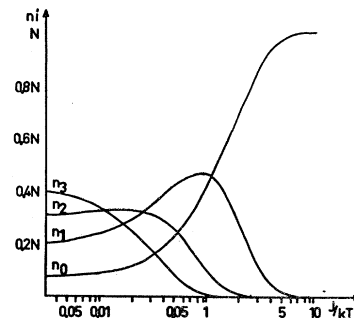

FIG. 12. Variations of the populations $n_0 \, n_1 \, n_2 \, n_3$ of the 4 sublevels of an antiferromagnetic pair, versus $1/T$.

[4] A. Hadni, G. Morlot, and P. Strimer, Compt. Rend. **258**, 515–518 (1964).
[5] P. Kisliuk, A. L. Schawlow, and M. D. Sturge, in *Quantum Electronics, Third Symposium* (Columbia University Press, New York, 1964), p. 725.

state of a pair of ions, coupled either antiferromagneti-cally or ferromagnetically. In each case, there are four possibilities for coupling two ions of spin $\frac{3}{2}$, leading to a total spin $S=0$, 1, 2, and 3. In a first approximation they take a quadratic isotropic exchange energy $H=J(\mathbf{S_1S_2})$, with $J=33$ cm^{-1} for the antiferromagnetic coupling, and in that case the positions of the 4 levels are $0-J=33-3J=99$ and $6J=198$ cm^{-1}. The observed far-infrared lines are interpreted as the $S=0\rightarrow 1$ and $S=0\rightarrow 2$ transitions. The $S=0\rightarrow 3$ would lie at 198 cm^{-1}, where the lattice absorption is considerable. Figures 12 and 13 give the behavior of the population for every level versus temperature, in each type of coupling, calculated from the partition functions. There is a drastic change of the population n_0 of the lower level only in the first type, and it explains quite well the observed variations of intensities of both lines with temperature.[4] The contribution of ferromagnetic pairs would give two lines at 35 and 42 cm^{-1}, which could be mixed with the antiferromagnetic one at 33 cm^{-1}. That would explain the slightly higher wave number observed (37 cm^{-1}), but this contribution is certainly small, and a check at 21 cm^{-1} is planned.

Recently, Kisliuk[6] has considered a more refined antiferromagnetic coupling with a quite different J

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[6] P. Kisliuk, Appl. Phys. Letters 3, 215 (1963).

Fig. 13. Variations of the populations $n_0\,n_1\,n_2\,n_3$ of the 4 sublevels of a ferro-magnetic pair, versus $1/T$.
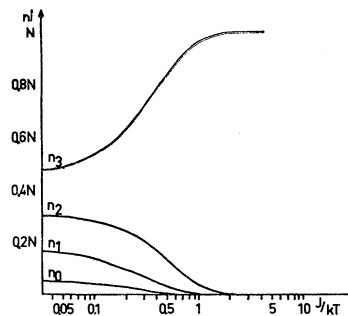
($J=11$ cm^{-1}) and a small biquadratic term: $H=J(\mathbf{S_1S_2})-j(\mathbf{S_1S_2})^2$, with $j/J=2\%$. The new positions of the 4 levels are now 0, 10.3, 32.7, and 67.9 cm^{-1}. They are quite different, but there are so many lines in the red that this scheme is also possible. However, the far-infrared spectra are strikingly in favor of the first one, and are impossible to explain with the second: There is a line at 100 cm^{-1}; there is none near 68 cm^{-1}.

ACKNOWLEDGMENTS

Anisotropic Lattice Absorption by Needle-Shaped Crystals

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Infrared absorption by small needle-shaped ionic crystals of cubic structure has recently been found to be anisotropic. In this note, a single strand is used as a limiting model for such a crystal, and the calculated ab-sorption in both directions is shown to be in qualitative agreement with observations on lithium fluoride. Features of absorptions to be expected from other crystals are discussed.

RECENTLY, Hass[1] prepared small needle-shaped lithium fluoride crystals by evaporating a thin film of lithium fluoride onto an optical grating (rather than onto a plane surface as is usual). The grating spacing, and hence the width of the resulting crystals, was small compared to the infrared absorption wavelength. The resulting absorption was found to be strongly anisotropic.[2]

We may summarize the experimental results by re-

ferring to the somewhat idealized rod-shaped crystals of Fig. 1. Let the light wave propagate in the z direction (into the paper); then the "usual" sharp absorption is found if the light is polarized in the x direction (parallel to the long edge of the crystal), but a broad absorption shifted to a higher frequency is found if the light is polarized in the y direction (perpendicular to the long edge of the crystal).

The simplest, and purely qualitative, theoretical

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[1] M. Hass, Proceedings of the Far Infrared Physics Symposium, Riverside, California, January 1964 (unpublished).
[2] Anisotropic Absorption by Needles of NiSb has also recently been reported by B. Paul and H. Weiss, Solid State Electron (to be published). D. W. Berreman, Phys. Rev. 130, 2193 (1963) has ob-served similar anisotropy and polarization dependence in the absorption of obliquely incident beams by thin films.
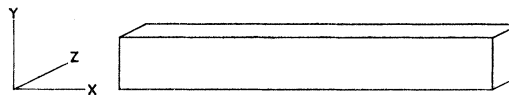

Fig. 1. Model of a needle-shaped crystal.