a priori reason to assume that throughout the sequence of europium terminal levels the pair dipole moment from either $2\bar{A}$ or $\bar{E}$ will be systematically larger than the other. We find that the ratio of the total intensities from the two ${}^2E_g$ levels for nine terminal levels, which were chosen primarily because their intensities could be accurately determined, is equal to the Boltzmann factor.

IV. SUMMARY

Europium-terminated chromium emission has now been observed in $EuAlO_3$ and $Eu_3Ga_5O_{12}$. Chromium emission terminating on the levels of terbium in $TbAlO_3$ has also been found and this will be reported in a future paper.[26] The sidebands are the electronic analogs of phonon-assisted emission and are closely related to the magnon sidebands observed in antiferromagnets. By analogy with the theory of magnon sidebands, we have argued that the exchange interaction between the chromium and europium ions leads to a spin-dependent electric dipole moment. An important feature of the present theory is the requirement of anisotropic exchange for both the chromium and europium ions, and the method of pair emission appears as an exceedingly attractive technique for studying these complex interactions.

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Line Strengths of the ${}^6P$ Multiplets of Gd^{3+} in CaF_2 at Cubic Sites*

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The line strengths of the purely magnetic dipole transitions from the nominally ${}^8S_{7/2}$ ground state of Gd^{3+} to the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ multiplets are calculated to be in the ratio of 1.77:1, in agreement with data on the cubic-site spectra of CaF_2:Gd^{3+}. The intermediate coupling calculation gives a ${}^6P_{7/2}$ oscillator strength of 6.35×10^{-8}. Longitudinal and transverse Zeeman measurements confirm the magnetic dipole transition character.

THE introduction of Gd^{3+} into a divalent-cation site in CaF_2 requires the presence of an additional charge to maintain over-all electrical neutrality. The location of this compensating ion will determine the symmetry of the local electrostatic field. A cubic field of eightfold coordination (O_h) results from a compensating ion lying further than two lattice constants from the Gd^{3+}. The optical spectra of the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ cubic-crystal-field multiplets have been identified by the use of EPR studies of the ground state in conjunction with heat treatment of the samples to vary the relative abundance of the sites.[1,2] Recent Zeeman measurements[3] have confirmed these results and identified the irreducible representations of the excited crystal-field levels for the cubic site. In this short note, the line strengths are examined.

Figure 1 shows the ${}^6P$ multiplet spectra of CaF_2: Gd^{3+}. The levels belonging to the cubic site are identified by vertical lines of length proportional to the calculated strengths. The measured and computed values are given in Table I.

For an ion in a static electric field of cubic symmetry, no first-order mechanism exists for the introduction of opposite parity character into the states of a single configuration ($4f^7$ in this case). Therefore, only mag-

Table I. Summary of CaF_2: Gd^{3+} cubic-site data.

Multiplet	$\int\alpha(\bar{\nu})d\bar{\nu}$ [a] (cm^{-2})	Energy (cm^{-1}) $\bar{\nu}_0$	Rep	$({}^8S_{7/2}\|\mathbf{L}+2\mathbf{S}\|{}^6P)$	Calculated oscillator strength[b] ($\times10^8$)
${}^6P_{7/2}$	0.18 0.35 0.20	32 035.8 32 051.1 32 092.8	${}^2\Gamma_6$ ${}^4\Gamma_8$ ${}^2\Gamma_7$	−0.5204	6.35
${}^6P_{5/2}$	0.26 0.13	32 637.6 32 653.8	${}^4\Gamma_8$ ${}^2\Gamma_7$	0.3873	3.58

[a] Data for a 0.5-mole % total Gd^{3+} sample in which about 25% of the Gd^{3+} is in the cubic site.

[b] In the first-order approximation the line-strength ratios are 1:2:1 and 2:1 for the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ multiplets, respectively.

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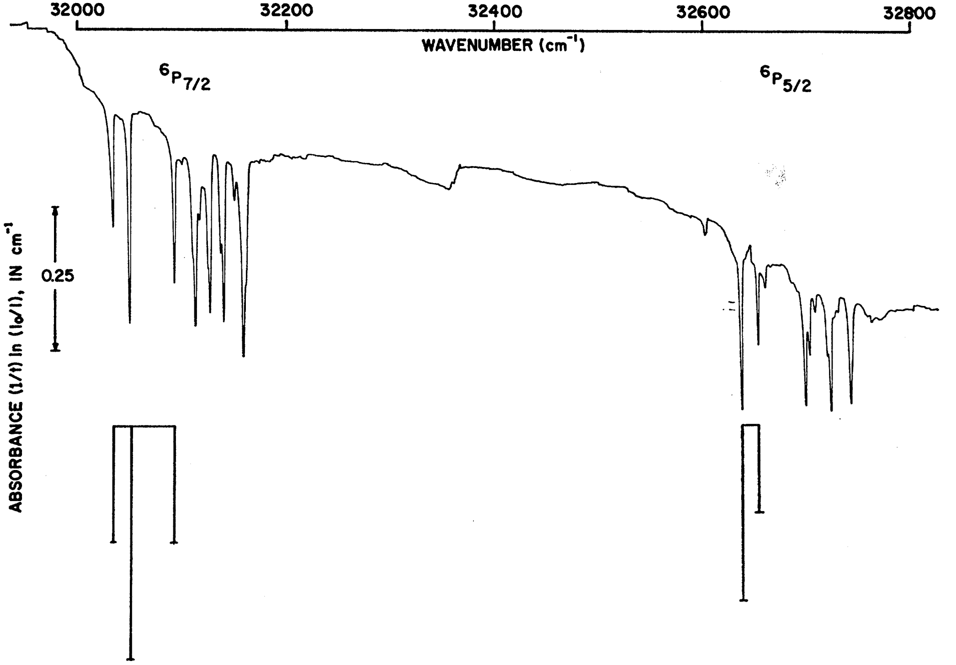

FIG. 1. 77°K absorption spectra of CaF_2:Gd^{3+} (0.4-mole % nominal Gd^{3+} doping). The transitions associated with ions in cubic sites are indicated by vertical lines whose length is proportional to the calculated strength. Within each multiplet each eigenstate contributes equally in first order to the line strength, so that the $^4\Gamma_8$ appears twice as intense as the $^2\Gamma_6$ and $^2\Gamma_7$. Approximately 25% of the Gd^{3+} is in the cubic site.

netic dipole or electric quadrupole f-f transitions are allowed. This assumption was verified by comparison of longitudinal and polarized transverse Zeeman spectra. The $^6P_{5/2}$ cubic site is shown in Fig. 2 as typical data. Since the π_{ed} transverse spectra coincide with the longitudinal patterns, the transitions are magnetic dipole.[4]

Magnetic dipole transitions between the states of f^N are parity-allowed, and the line strengths may be computed without the use of adjustable parameters. Because the ground-state splitting[5] is only 0.149 cm^{-1}, the spectroscopic stability criterion is satisfied even at 77°K, and measured values are readily compared to calculations. The oscillator strength is defined as[6]

$$P_{md}=4.028\times10^{-11}n\bar{\nu}_0$$
$$\times|(f^N[\alpha LS]JJ_z|\mathbf{L}+g_s\mathbf{S}|f^N[\alpha LS]'J'J_z')|^2/(2J+1),$$

where n is the index of refraction (1.43 for CaF_2), $\bar{\nu}_0$ the transition energy (cm^{-1}); **L** and **S** are the orbital and spin angular momentum operators. The matrix elements may be computed by tensor operator methods.[6] The $\Delta J=\pm1$ selection rule is closely obeyed and no $^6P_{3/2}$ transitions are observed. The intermediate coupling vectors were obtained from the free-ion Hamiltonian due to Judd *et al.*[7] with the first-order J_z composition of the Stark multiplets as given by Lea *et al.*[8] For cubic-crystal-field manifolds with J less than $\frac{7}{2}$, the J_z composition is independent of the field parameters and gives rise to equal magnetic dipole contributions from each eigenstate. The reduced matrix elements obtained from the complete set of αLS states for the free ion are given in Table I.

The ratio of $^6P_{7/2}$ to $^6P_{5/2}$ magnetic dipole strength is calculated to be 1.77:1 in agreement with the value of 1.79:1 found by Gilfanov *et al.*,[9] and with measurements made in this laboratory.[10] The total $^8S_{7/2}$ to $^6P_{7/2}$ strength is computed to be 6.35×10^{-8} for a purely magnetic dipole transition, again in agreement with the cubic-site observations.[9] The electric quadrupole contribution is less than 1% of this value. The fluorescence lifetime of the $^6P_{7/2}$ to $^8S_{7/2}$ transition is 10.8 msec in agreement with the measured values.[9]

The samples were grown by OPTOVAC Inc. using the Stockbarger-Bridgman method in vacuum. Following a slow annealing, right circular cylinders approximately 1 cm long and 1 cm diam were cut with the

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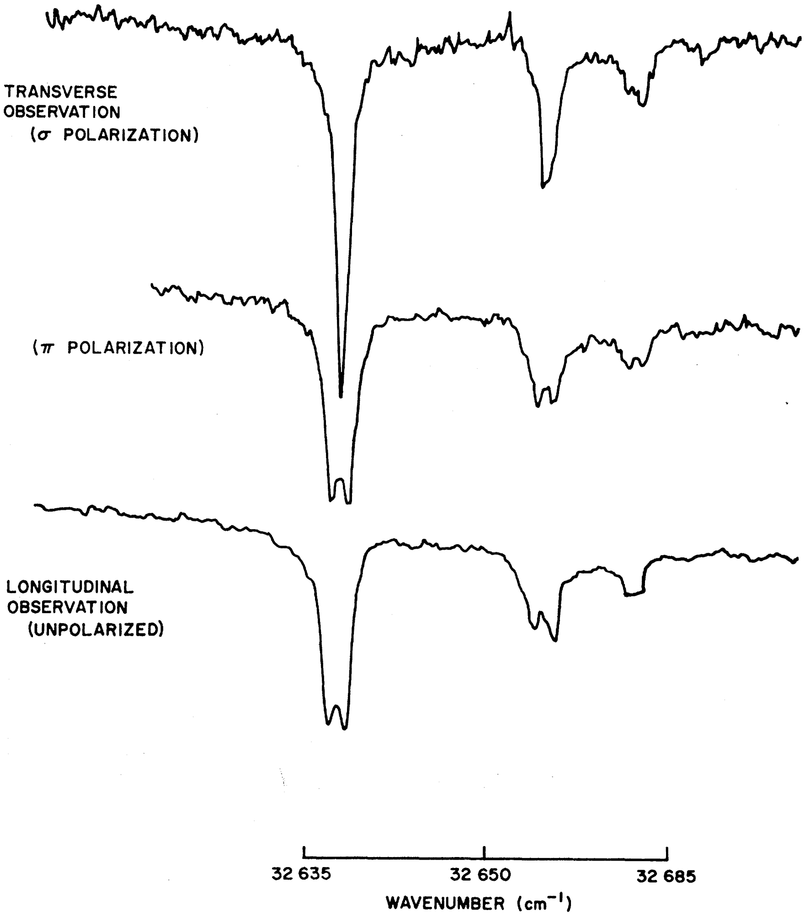

FIG. 2. Transverse and longitudinal Zeeman absorption spectra of the cubic-crystal-field split $^6P_{5/2}$ multiplet of Gd^{3+} in CaF_2. The magnetic field is 6.1 kOe directed along the [001]. In the transverse experiment, radiation is incident normal to the magnetic field and polarized with the electric vector perpendicular (σ) or parallel (π) to the magnetic field. Sample temperature is 77°K.

[110] along the cylindrical axis. A Jarrell-Ash 3.4-m spectrograph with resolving power of better than 450 000 produced a second-order reciprocal dispersion of 0.8 Å/mm. The spectrograph slit is 20 μ wide and has a negligible effect on the line shape and intensity measurements. Density measurements of Kodak *V-F* plates were made with a Joyce-Loebel microdensitometer.

Because a site of cubic symmetry is possible, the alkaline-earth fluorides doped with Gd^{3+} (or any tripositive rare earth) offer a unique opportunity to test line-strength calculations. The cubic site allows the magnetic dipole contribution to be measured independently of the electric dipole strength,[11,12] which may be operative for ions in sites of lower symmetry (C_{4v},C_{3v},C_s) in the same hosts.[1,2]

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