

¹⁷ 567 (1966); *Appl. Phys. Letters* **9**, 265 (1966).

¹⁷R. G. Sachs and D. L. Dexter, *J. Appl. Phys.* **21**, 1304 (1950).

¹⁸P. H. Cutler and J. J. Gibbons, *Phys. Rev.* **111**,

394 (1958).

¹⁹P. H. Cutler and R. H. Good, Jr., *Phys. Rev.* **104**, 308 (1956).

Excited-State Absorption Cross Sections for the Cr³⁺ Ion in MgO and Spinel

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We have calculated numerically the magnetic dipole absorption cross sections for the excited-state transitions t_2^3 $^2E \rightarrow t_2^3$ 2T_2 and t_2^3 $^2T_1 \rightarrow t_2^3$ 2T_2 in centrosymmetric MgO:Cr³⁺ and MgAl₂O₄:Cr³⁺. This was done by using a parametrized ligand-field model in which the parameters are determined by the zero-field energies. The dominant contribution to the $^2E \rightarrow ^2T_2$ absorption comes from Coulomb admixture of $t_2^3 e$ and t_2^3 terms, whereas the spin-orbit interaction contributes substantially to the $^2T_1 \rightarrow ^2T_2$ cross section. The values obtained provide a reliable guide to the assignment of recent $^2E \rightarrow ^2T_2$ excited-state absorption measurements in MgO:Cr³⁺.

I. INTRODUCTION

The measurement of absorption from excited metastable states in solids is becoming an important spectroscopic technique. One of the main reasons for this is that it enables the observation of excited states which may be forbidden or only weakly allowed in transitions from the ground state. For example, transitions from the t_2^3 4A_2 ground state of d^3 impurity ions (e.g., Cr³⁺) to other nominally t_2^3 levels (2E , 2T_1 , and 2T_2) are essentially spin forbidden and derive their intensity from spin-orbit admixture of $t_2^3 e$ 4T_2 . On the other hand, transitions within the doublet terms are spin allowed and have much higher cross sections than those from the ground state. When the impurity-ion site lacks a center of symmetry, the absorption will, almost always, be electric dipole (ED) due to the admixture of odd-parity states into the d -like states. On the other hand, for ions in centrosymmetric sites where ED transitions are forbidden, the zero-phonon lines will be much weaker and magnetic dipole (MD) in nature. A number of experimental studies of excited-state absorption have been made, almost all on ruby (Al₂O₃:Cr³⁺),¹⁻⁸ where the Cr³⁺ site is not centrosymmetric. In this case, the zero-phonon lines are electric dipole and have been definitely identified only for the t_2^3 2E , $^2T_1 \rightarrow ^2T_2$ transitions,³⁻⁵ which have an integrated absorption coefficient per ion of about 10^{-17} cm (oscillator strength $f = 5 \times 10^{-6}$). Tentative assignments of the zero-phonon transitions $^2E \rightarrow ^2A_1$ and 2A_2 have also been made.⁸

A theoretical calculation of ED absorption cross sections is difficult because of a lack of knowledge

of the detailed nature of the odd-parity states involved and of the odd-parity crystal field. Thus in the perturbation treatment by Shinada *et al.*,⁶ the excited-state absorption coefficients in ruby are obtained in terms of a number of unknown parameters, which are the reduced matrix elements of the odd-parity crystal field (which produces the mixing leading to the ED transitions). This means that the relative absorption strengths cannot be calculated uniquely, and the absolute strengths can only be roughly estimated.

The complications outlined above for ED calculations do not arise for MD absorption which is parity allowed within the d^3 configuration. We report here the first numerical calculation of MD excited-state absorption coefficients. By transforming the MD operator to the basis of the eigenvectors of the impurity Hamiltonian [Eq. (1)], we have obtained absolute absorption coefficients for the t_2^3 $^2E_g \rightarrow t_2^3$ $^2T_{2g}$ and t_2^3 $^2T_{1g} \rightarrow t_2^3$ $^2T_{2g}$ transitions for two centrosymmetric $3d^3$ systems, viz., Cr³⁺ in the cubic sites of MgO, and Cr³⁺ in the trigonal sites of spinel (MgAl₂O₄ or ZnAl₂O₄). The only parameters involved are those determining the zero-field energies and g values, and these can be overdetermined without reference to experimental intensity measurements. We find that the integrated absorption coefficient per ion for the t_2^3 $^2E_g \rightarrow ^2T_{2g}$ transition is $\approx 10^{-19}$ cm ($f = 5 \times 10^{-6}$). Reliable analytical perturbation expressions for the MD intensities cannot be obtained. In Sec. II the dependence of the MD line strengths on the zero-field parameters is explored, and it is found that the t_2^3 $^2E \rightarrow ^2T_2$ strength is almost independent of trigonal and spin-orbit

parameters, but this is not true of the $t_2^{3/2}T_1 \rightarrow ^2T_2$ line strength.

II. CALCULATION OF MD TRANSITION PROBABILITIES

The transition probabilities for excited-state absorption were calculated following a method recently described by the author.⁹ Matrix elements of a ligand-field Hamiltonian for the Cr³⁺ impurity ion were calculated in a weak-field trigonal basis $|\alpha SLJ\hat{\Gamma}_T\hat{\gamma}_T\rangle$ within the 120 states of the d^3 configuration.¹⁰ $\hat{\Gamma}_T$ and $\hat{\gamma}_T$ label the representations and components of any of the five trigonal double groups D_{3d}^* , C_{3h}^* , D_{3d}^* , C_{3v}^* , and C_{3h}^* . The Hamiltonian, which can be written schematically to show the parameter dependence as

$$\mathcal{H} = \mathcal{H}_1(\Delta) + \mathcal{H}_2(B, C) + \mathcal{H}_3(v, v') + \mathcal{H}_4(\xi), \quad (1)$$

included cubic crystal field, single-ion Coulomb, trigonal crystal field, and spin-orbit terms. In trigonal symmetry, \mathcal{H} factorizes into three blocks \bar{E}_+ , \bar{E}_- , and $2\bar{A}$ of order 39, 39, and 42, respectively. For Cr³⁺ in the cubic sites of MgO, $v = v' = 0$. Under these conditions, some \bar{E} doublets become Γ_6 , some become Γ_7 , and pairs of \bar{E} , $2\bar{A}$ become degenerate as Γ_8 .

The parameters of Eq. (1) were overdetermined by analysis of the optical and microwave energies and g values.^{9,11} Apart from v and v' , they were

found to vary little over a number of Cr³⁺ impurity systems. The energies and g values agreed with available experimental data to within about 10%, so the zero-field eigenvectors of \mathcal{H} have a similar reliability. These eigenvectors were obtained by numerical diagonalization, and will be denoted $|\alpha SLJ\hat{\Gamma}_T\hat{\gamma}_T\rangle$, where αSL runs over the terms of d^3 . These define an intermediate coupling numerical basis which will serve as the zero-order basis for a perturbation calculation of the transition probabilities. The line strength for transitions between two Kramers's doublets $\hat{\Gamma}_T$ and $\hat{\Gamma}'_T$, resulting in absorption of incident radiation whose \vec{H} field is in the direction of the unit vector \vec{e}_κ , is defined as

$$s_\kappa(\omega\hat{\Gamma}_T; \omega'\hat{\Gamma}'_T) = \beta^2 \sum_{\hat{\gamma}_T\hat{\gamma}'_T} |\langle \omega\hat{\Gamma}_T\hat{\gamma}_T | \vec{\mu} \cdot \vec{e}_\kappa | \omega'\hat{\Gamma}'_T\hat{\gamma}'_T \rangle|^2. \quad (2)$$

The magnetic dipole operator $\vec{\mu}$ is equal to $(k\vec{L} + g_s\vec{S})$, where k is the orbital reduction factor which, for fairly ionic solids such as we are discussing here, is about 0.7. The s_κ are independent of level populations. Matrix elements of $\vec{\mu}$ were calculated in an $|\alpha SLJ\hat{\Gamma}_T\hat{\gamma}_T\rangle$ basis, and a numerical calculation of the s_κ was made by transforming $\vec{\mu}$ to the basis of the eigenvectors of \mathcal{H} . Thus, we have

$$\begin{aligned} \langle \omega\hat{\Gamma}_T\hat{\gamma}_T | \mu_\kappa | \omega'\hat{\Gamma}'_T\hat{\gamma}'_T \rangle = & \sum_{\alpha SLJ; \alpha' S'L'J'} \langle \omega\hat{\Gamma}_T\hat{\gamma}_T | \alpha SLJ\hat{\Gamma}_T\hat{\gamma}_T \rangle \langle \alpha SLJ\hat{\Gamma}_T\hat{\gamma}_T | \mu_\kappa | \alpha' S'L'J'\hat{\Gamma}'_T\hat{\gamma}'_T \rangle \\ & \times \langle \alpha' S'L'J'\hat{\Gamma}'_T\hat{\gamma}'_T | \omega\hat{\Gamma}_T\hat{\gamma}_T \rangle \delta_{SS}, \delta_{LL'} . \end{aligned} \quad (3)$$

This yields s_κ for any magnetic dipole transition within the manifold of d -like states. For high-energy transitions ($\geq 30\,000 \text{ cm}^{-1}$ above 2E) the final states will have an appreciable admixture of charge-transfer states, and transition probabilities calculated from Eq. (3) are expected to be less reliable. We are interested in the cases where the initial states $\hat{\Gamma}'_T$ are $t_2^{3/2}\bar{E}$, \bar{E} , $2\bar{A}$; $t_2^{3/2}T_1\bar{E}_a$, \bar{E}_b , $2\bar{A}$ and the final states $\hat{\Gamma}_T$ are $t_2^{3/2}T_2\bar{E}_a$, \bar{E}_b , $2\bar{A}$, these transitions occurring around 5000 – $10\,000 \text{ cm}^{-1}$. The t_2^3 labels are approximate, but useful for identifying the cubic terms. The $t_2^{3/2}E \rightarrow t_2^{3/2}T_1$ transitions have not been observed since they lie in a region of the spectrum (400 – 600 cm^{-1}) where detectors are less sensitive and there is competitive absorption from one-phonon processes. Line strengths involving cubic Γ_8 levels are obtained by summing over the doublet line strengths of Eq. (2). For example, we have

$$s_\kappa(\omega\Gamma_8; \omega'\Gamma'_8) = \sum_{\hat{\Gamma}_T=\bar{E}, 2\bar{A}; \hat{\Gamma}'_T=\bar{E}, 2\bar{A}} s_\kappa(\omega\hat{\Gamma}_T; \omega'\hat{\Gamma}'_T), \quad (4)$$

and, of course,

$$s_x = s_y = s_z .$$

In general, only the matrix of μ_z is diagonal in the quantum numbers $\hat{\Gamma}_T\hat{\gamma}_T$. For $\mu_{x,y}$, there are matrix elements connecting \bar{E}_+ , \bar{E}_- , and $2A$. The integrated absorption coefficient per ion for transitions from 2E and 2T_1 (which are in thermal equilibrium) depends on the thermal populations of the sublevels, so that for absorption from each of the initial states $\hat{\Gamma}'_T$

$$N^{-1} \left(\int k_\sigma d\sigma \right)_* (\hat{\Gamma}_T; \hat{\Gamma}'_T) = \frac{8\pi^3\sigma\eta}{hc} \frac{N'}{Ng'} s_\kappa(\hat{\Gamma}_T; \hat{\Gamma}'_T) , \quad (5)$$

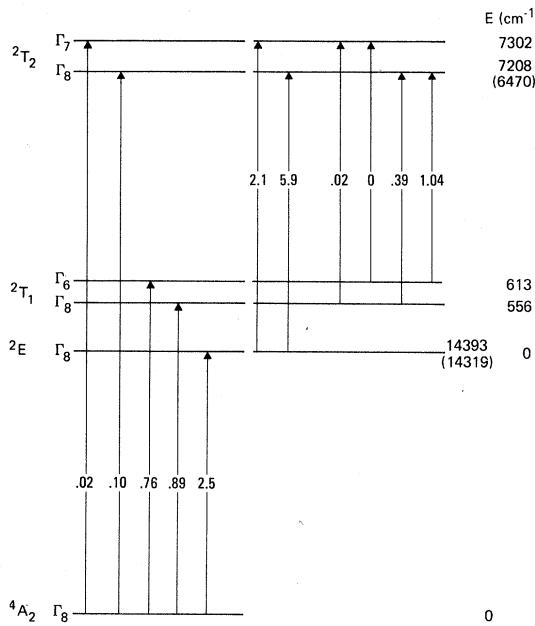


FIG. 1. Energy-level diagram and unweighted integrated absorption coefficients per ion (in units of 10^{-20} cm) for transitions within the nominally t_2^3 levels of MgO:Cr^{3+} . For absorption at finite temperatures the numbers given must be weighted by the statistical fraction of ions in a given initial state. For temperatures below $\sim 150^\circ\text{K}$, less than 1% of the ions will be in the 2T_1 state and the weighting factor for $^2E \Gamma_8$ is unity. The parameters used in the calculation are the same as in Ref. 9, viz., $\Delta=16\,600$, $B=650$, $C=3200$, $\zeta=225\text{ cm}^{-1}$. Calculated energies (not to scale) are shown, with experimental values, where known, in parentheses.

where σ is the transition energy in cm^{-1} , k_σ is the absorption coefficient at energy σ , η is the refractive index, g' is the degeneracy of $\hat{\Gamma}'_T$, and N'/N is the Boltzmann factor expressing the fraction of ions in the initial states $\hat{\Gamma}'_T$. In cubic symmetry it is necessary to sum over $\hat{\Gamma}_T$, $\hat{\Gamma}'_T$ in a way analogous to Eq. (4), remembering that g' is 4 for a Γ_8 initial state.

Figures 1 and 2 show the energy levels and unweighted (i.e., omitting the temperature-dependent factor N'/N) integrated absorption coefficients per ion calculated for MgO:Cr^{3+} and $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ (or $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$), respectively. In Fig. 1 absorption strengths for transitions from the ground state are also shown for comparison. These results show that the $^2E \rightarrow ^2T_2$ transition is expected to be about 60 times stronger than the ground-state transition $^4A_2 \rightarrow ^2T_2$. This means that with the typical excited-state populations which can be achieved, it should be easier to observe transitions to 2T_2 from the excited 2E level than it is from the ground state.

Klauminzer¹² has recently obtained preliminary measurements of excited-state absorption in the

region of $t_2^3 \rightarrow ^2T_2$ in MgO:Cr^{3+} . While a definite assignment of the lowest observed transition has not yet been made, its strength ($N^{-1} \int k_\sigma d\sigma \approx 10^{-18}$ cm, cf. our calculated value of 8×10^{-20} cm) suggests that it is not the MD zero-phonon line. It is worthwhile to comment here on the reliability of our calculations and what can be hoped for by way of agreement with experimental data. The model we use assumes that the Cr^{3+} orbitals in the crystal transform like d orbitals under the site group, and does not include explicit admixture of charge-transfer states. These assumptions should be good in ionic solids for energies in the visible region and lower. By diagonalizing \mathcal{H} within the 120 d -like states of d^3 we calculate the consequences of the model in some detail. For Cr^{3+} in the cubic sites of MgO , the four parameters Δ , B , C , and ζ of \mathcal{H} (with B , C , and ζ constrained to be $\sim 25\%$ below their free-ion values) give the energies of the t_2^3 , 2E , $t_2^3 \rightarrow ^2T_2$, $t_2^3 \rightarrow ^4T_2$, and $t_2^3 \rightarrow ^4T_1$ terms and $g(^4A_2)$, $g(^2E)$ to better than 10%. Using the eigenvectors of \mathcal{H} determined by these parameters, we calcu-

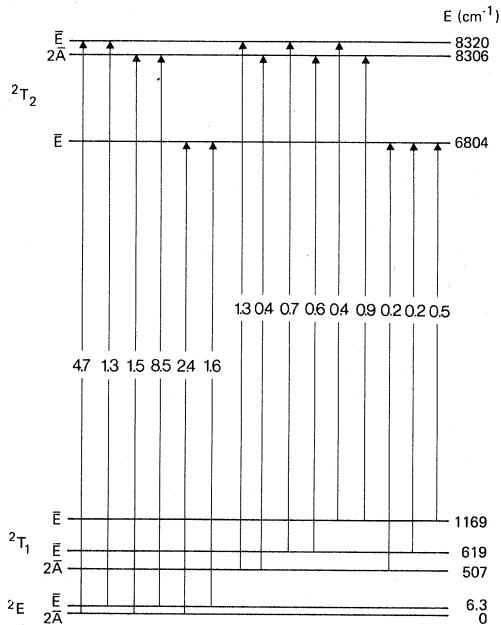


FIG. 2. Energy-level diagram and unweighted integrated absorption coefficients per ion (in units of 10^{-20} cm) for excited-state transitions in $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ (or $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$). The values given are averaged over all polarizations, as required by the cubic symmetry of the spinal lattice. Because of the larger number of transitions, we have omitted the ground-state absorption strengths. These may be found in Ref. 9. The parameter values determined by zero-field energies (Refs. 9 and 11) are $\Delta=18\,250$, $B=700$, $C=3200$, $\nu=-200$, $\nu'=-1700$, and $\zeta=250\text{ cm}^{-1}$. The population weighting factor (N'/N) at $T=0^\circ\text{K}$ is unity for $^2E 2\bar{A}$ and zero for all others. For $T \gtrsim 100^\circ\text{K}$ but low enough to depopulate 2T_1 , N'/N is $\frac{1}{2}$ for both $^2E 2\bar{A}$ and $^2E \bar{E}$.

lated⁹ the $^4A_2 \rightarrow ^2E$ absorption cross section (which goes like ζ^2) within 20% of the experimental value. In that case, the assignment to zero-phonon lines of Cr^{3+} in cubic sites was unambiguous as the lines are sharp enough to allow polarized Zeeman measurements to be made.¹³ The transition probabilities are a quadratic function of small changes in the model parameters and hence are more sensitive tests of the parameters than are the energies. For levels which do not couple strongly to phonons, we expect the method used here to give absorption strengths to better than a factor of 2 or 3 after taking account of the difficulty in measuring the absolute number of excited impurity ions and the Condon factor, which reduces the intensity of the zero-phonon lines. Failure to achieve this would indicate that the levels have substantial amounts of non-*d*-character.

Experimental measurements on the spinel system have not yet been made, but measurements of the *R*-line excitation spectrum¹¹ indicate that the $^2E \rightarrow ^2T_2$ transition lies at about 7450 cm^{-1} . The spinel structure has cubic symmetry (O_h^7), but the Cr^{3+} sites are trigonal. Therefore, we have averaged the absorption coefficients over the three polarization directions.

The numerical calculation we have described has the disadvantage of not leading to analytical expressions for the absorption strengths in terms of the model parameters. Such expressions can, in principle, be obtained by a perturbation calculation using strong cubic field zero-order states, i.e., those which diagonalize $\mathcal{H}_1(\Delta)$, the largest term in the Hamiltonian. However, the $t_2^3 \cdot ^2T_1 \rightarrow t_2^3 \cdot ^2T_2$ absorption strengths vanish in first order and the convergence of the perturbation expansion is too slow to provide reliable expressions. This has also been found to be the case for *g* values and zero-field splittings.⁹ Some insight into the mechanisms giving intensity to the excited-state absorption can be obtained by studying the parameter dependence of the line strengths. Table I shows the line strengths [which are related to the integral absorption coefficients per ion by Eq. (5)], including a number of limiting cases in which the parameters describing the strength of the trigonal field (v, v') and spin-orbit coupling (ζ) are set equal to 0. Several conclusions can be drawn from this. The $^2E \rightarrow ^2T_2$ absorption strength is essentially independent of v, v' , and ζ and hence is insensitive to distortion of the local environment around the Cr^{3+} impurity ions. Instead, the absorption occurs because of Coulomb admixture of higher 2E and 2T_2 terms into the nominally t_2^3 levels. It would, therefore, be possible to obtain reliable values by a simpler

TABLE I. Integrated line strengths $S'_k = \beta^{-2} S_k$, tabulated to show the parameter dependence of the $^2E \rightarrow ^2T_2$ and $^2T_1 \rightarrow ^2T_2$ intensity in $MgO:Cr^{3+}$ and $MgAl₂O₄:Cr³⁺$.

MgO:Cr ³⁺		MgAl ₂ O ₄ :Cr ³⁺	
S'_k		$\frac{1}{3} \sum_k S'_k$	
$^2E \rightarrow ^2T_2$		$^2T_1 \rightarrow ^2T_2$	
b	0.235	a	0.257
	$\zeta = 0$	$v = v' = 0$	0.233
$\zeta = 0$	0.211	$v = v' = \zeta = 0$	0.209
b	0.030	a	0.078
	$\zeta = 0$	$v = v' = 0$	0.034
$\zeta = 0$	0.014	$v = v' = \zeta = 0$	0.014

^aFor the spinel parameters of Fig. 2.

^bFor the MgO parameters of Fig. 1.

cubic calculation with $\zeta = 0$. The intensity distribution among the components of 2E and 2T_2 could then be obtained by an application of the Wigner-Eckart theorem

$$\langle ^2E \gamma | \vec{\mu}(T_{1g}) | ^2T_2 \gamma' \rangle = V \begin{pmatrix} E & T_2 & T_1 \\ \gamma & \gamma' & \bar{\gamma} \end{pmatrix} \langle ^2E | \vec{\mu}(T_{1g}) | ^2T_2 \rangle, \quad (6)$$

with the components $\gamma, \gamma', \bar{\gamma}$ chosen to transform irreducibly in the site group. This is not the case, however, for the $^2T_1 \rightarrow ^2T_2$ line strengths which are rather sensitive to both the trigonal-field and spin-orbit coupling.

III. CONCLUSION

Using a parametrized ligand-field model in which the parameter values are fixed by the zero-field energies, we have calculated line strengths and integrated absorption coefficients for excited-state absorption within the nominally t_2^3 levels of Cr^{3+} ions in MgO and spinel. This was done by numerically transforming the MD operator to a basis of the zero-field eigenstates and does not require the introduction of any additional parameters. From previous experience with *g* values and ground-state absorption strengths,⁹ we expect this to give reliable results since the t_2^3 levels couple only weakly to phonons. Thus, the results presented here should be of considerable assistance in interpreting present¹² and future measurements of excited-state absorption.

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¹T. H. Maiman, Phys. Rev. Letters 4, 564 (1960).

²F. Gires and G. Mayer, Compt. Rend. 254, 659 (1962).

³T. Kushida, J. Phys. Soc. Japan 20, 619 (1965).

⁴G. K. Klauminzer, P. L. Scott, and H. W. Moos,

Phys. Rev. 142, 248 (1966).
⁵T. Kushida, J. Phys. Soc. Japan 21, 1331 (1966).
⁶M. Shinada, S. Sugano, and T. Kushida, J. Phys. Soc. Japan 21, 1342 (1962).
⁷J. W. Huang and H. W. Moos, Phys. Rev. 173, 440 (1968).
⁸T. M. Dunn and A. H. Francis, Phys. Rev. Letters 25, 705 (1970).
⁹R. M. Macfarlane, Phys. Rev. B 1, 989 (1970).
¹⁰R. M. Macfarlane, J. Chem. Phys. 39, 3118 (1963).
¹¹D. L. Wood, G. F. Imbusch, R. M. Macfarlane, P. Kisliuk, and D. M. Larkin, J. Chem. Phys. 48, 5255 (1968).
¹²G. K. Klauminzer, Ph.D. dissertation, Stanford University (unpublished); Microwave Laboratory Report No. MLR 1878 (unpublished).
¹³S. Sugano, A. L. Schawlow, and F. Varsanyi, Phys. Rev. 120, 2045 (1960).

Electron Spin Resonance of Gadolinium-Hydride and Gadolinium-Deuteride Ion Pairs in Calcium Fluoride Crystals

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Electron-spin-resonance measurements of gadolinium-hydride and gadolinium-deuteride ion pairs of tetragonal symmetry in crystals of calcium fluoride are reported. The parameters of the spin Hamiltonian for the ground state of the Gd^{3+} ion are determined. It is shown that the main parts of the $^8S_{7/2}$ and $^6P_{7/2}$ state splittings can be correlated and are due to the second-degree term in the crystal-field potential. The second-degree term is calculated using an "ionic" model including dipole moments of ions, and it is found to be in a reasonable accord with the experimentally derived value. Contributions to the isotope shift between the zero-field splittings of Gd^{3+} paired with hydride and with deuteride ions are calculated. The total value of the isotope shift estimated by using the ionic model appears to be one-quarter the magnitude of the observed shift and of opposite sign.

INTRODUCTION

An extensive study of rare-earth ions in hydrogenated calcium fluoride was performed recently by optical and infrared spectroscopy.¹ Trivalent rare-earth ions substituted into the lattice sites of divalent calcium ions may be charge compensated by hydride ions in interstitial lattice sites. It was found that some of these hydrogen ions are coupled with the trivalent rare-earth ions, producing pairs of tetragonal symmetry. It was shown that in such pairs the rare-earth ion is accompanied by the hydride ion in the nearest interstitial site of the lattice.

Both absorption and fluorescence spectra caused by transitions between the $^8S_{7/2}$ ground state and $^6P_{7/2}$ excited states of the Gd^{3+} -H⁻ pair have been reported. Likewise, the infrared spectrum caused by local modes of the H⁻ ion in this pair has been identified.¹ Recently, electrostatic parameters for the $4f^7$ configuration of the Gd^{3+} ion in a CaF₂ lattice were determined from the absorption spectrum down to 1350 Å.² In the light of this information, a measurement of the Gd^{3+} ground state by electron spin resonance (ESR) should be of interest. Moreover, the isotope shift of the zero-field splitting for Gd^{3+} -H⁻ and Gd^{3+} -D⁻ pairs could throw some new light on the origin of the electron-phonon

interaction between localized electronic states and vibrational states of the lattice. In fact, the very light H⁻ ions have strongly localized vibrational modes with frequencies higher than the vibrational bands of the host crystal. They may be represented by the simple model of a charged particle moving in the constant electrostatic field of the lattice with a very reasonable accuracy.

In this paper parameters of the spin Hamiltonian for the ground state of the Gd^{3+} -H⁻ pair and of the Gd^{3+} -D⁻ pair are reported. We shall endeavor to explain the zero-field splitting and its isotope shift in the limits of the so-called "ionic" model.

EXPERIMENTAL TECHNIQUES AND RESULTS

Crystals of CaF₂ containing 0.05% (molar concentration) of GdF₃ were obtained from the Hebrew University of Jerusalem. Hydrogen and deuterium were introduced into the crystals by the Hall and Schumacher method, as described by Jones *et al.*¹ After the hydrogenation period at 800 °C, the crystals were rapidly quenched to room temperature in order to prevent formation of complex Gd^{3+} -H⁻ clusters which confuse the spectrum.

The ESR measurements were made at room temperature using a Q-band spectrometer equipped with a rectangular cavity. The crystals were mounted on the cylindrical sample holder with the