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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 CaF$_2$ 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 CaF$_2$ containing 0.05% (molar concentration) of GdF$_3$ 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

$[1\bar{1}0]$ direction parallel to its axis. This is convenient because the spectra in both the [100] and [110] directions can be obtained by rotating the sample holder through 90°. Analysis of the spectrum of the hydrogenated and deuterated crystals was simplified by also examining the spectrum of a crystal treated in a mixed hydrogen-deuterium atmosphere and the spectrum of a completely untreated crystal.

In the untreated crystal we observed the spectra of Gd^{3+} ions in cubic sites,[3] the tetragonal spectra of Gd^{3+}-F^- pairs,[4] and the trigonal spectra of Gd^{3+}-O^{2-} pairs.[5] The intensities of the first two types are approximately the same, whereas the trigonal spectra are about ten times weaker. In hydrogenated crystals there was, in addition, a new tetragonal spectrum about 20 times less intense than that of the Gd^{3+}-F^- pairs and with linewidths of about 10 G. All lines of this new spectrum were doubled in the crystal treated with both hydrogen and deuterium. These spectra are evidently due to the tetragonal Gd^{3+}-H^- and Gd^{3+}-D^- pairs identified by Jones *et al.*[1] The spin Hamiltonian describing the two new spectra is assumed to be of the same form as previously used[4] for tetragonal Gd^{3+}-F^- pairs:

$$H = g\mu_B \vec{H}\cdot\vec{S} + B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4 \ , \quad (1)$$

which operates on the magnetic substates of spin $S=\frac{7}{2}$. The O_n^m are the usual spin-Hamiltonian operator equivalents.[6] Determination of the parameters B_n^m is aided by the knowledge that the first two terms in (1) are dominant, and that the first three O_n^m's have only diagonal elements and the last two only nondiagonal elements. Hence for $\vec{H}$ parallel to the tetragonal axis z, the energy levels, correct to first-order perturbation theory, are simple linear combinations of g, B_2^0, B_4^0, and B_6^0, and these parameters may be readily determined by solving the appropriate simultaneous equations. B_6^4 and B_4^4 only appear in second order for $\vec{H} \parallel z$, and their contribution to the energy levels is comparable with the experimental uncertainty. It is therefore impossible to accurately evaluate them in this orientation, so that the $\vec{H} \parallel x$ orientation was also studied. Under the transformation of axes $xyz \rightarrow z'x'y'$, the spin Hamiltonian (1) becomes, with respect to the new axes,[7]

$$\begin{aligned} H = g\mu_B \vec{H}\cdot\vec{S} &- B_2^0(\tfrac{1}{2}O_2^0 + \tfrac{3}{2}O_2^2) + B_4^0(\tfrac{3}{8}O_4^0 + \tfrac{5}{2}O_4^2 + \tfrac{35}{8}O_4^4) \\ &- B_6^0(\tfrac{5}{16}O_6^0 + \tfrac{105}{32}O_6^2 + \tfrac{63}{16}O_6^4 + \tfrac{231}{32}O_6^6) \\ &+ B_4^4(\tfrac{1}{8}O_4^0 - \tfrac{1}{2}O_4^2 + \tfrac{1}{8}O_4^4) \\ &- B_6^4(\tfrac{1}{16}O_6^0 + \tfrac{5}{32}O_6^2 - \tfrac{13}{16}O_6^4 + \tfrac{11}{32}O_6^6) \ . \qquad (2) \end{aligned}$$

For $\vec{H} \parallel z'$ (i.e., $\vec{H} \parallel x$) the energy levels contain B_4^4 and B_6^4 in first order as desired. Unfortunately, there are now large off-diagonal elements due to the $B_2^0O_2^2$ term. The procedure adopted to overcome this difficulty was as follows: The values of g, B_2^0, B_4^0, and B_6^0 determined previously for $\vec{H} \parallel z$ were substituted into Eq. (2), and that part of the spin Hamiltonian involving them was diagonalized by the computer and the eigenvectors found. The operators involving B_4^4 and B_6^4 in (2) were then transformed to the same eigenvector basis and considered as a perturbation to first order. The energy levels can thus be written as linear combinations of B_4^4 and B_6^4 and the values of these parameters can be obtained. Equations (1) and (2) implicitly assume $g_\parallel = g_\perp$. In order to verify this a correction term $\Delta g \mu_B H_{z'} S_{z'}$ was included as a small perturbation in (2) and Δg evaluated in the same manner as B_4^4 and B_6^4. It was found for both Gd^{3+}-H^- and Gd^{3+}-D^- that Δg was zero to within the experimental uncertainty, and hence $g_\parallel = g_\perp = 1.992 \pm 0.001$.

The calculated values of the B_n^m coefficients for Gd^{3+}-D^- and Gd^{3+}-H^- are presented in Table I. We also calculated the B_n^m coefficients for Gd^{3+}-F^- pairs by the same method of analysis and it can be seen that these are in close agreement with the previous results of Vinokurov *et al.*[4] The only notable difference is in the value of B_6^4. For $\vec{H} \parallel x$ we observed four ESR lines and thus obtained four simultaneous equations in two unknowns (B_6^4 and B_4^4). These were self-consistent and so our value of B_6^4 should be reliable. As a further test, the spin Hamiltonians, using the parameters quoted in Table I for Gd^{3+}-H^- and Gd^{3+}-D^-, were used to predict the magnetic field strengths at which transitions occur for $\vec{H} \parallel x$. Agreement with experimental field strengths was better than ± 2 G.

The procedure outlined in this section correctly gives the signs of all the quantities B_n^m relative to B_2^0, but does not give the actual sign of B_2^0. This has been determined for Gd^{3+}-F^- by measuring the relative intensities of the ESR lines at liquid-helium temperatures.[8] The values of B_2^0 for Gd^{3+}-H^- and Gd^{3+}-D^- have been assumed to be of the same sign as Gd^{3+}-F^- because of the very close resem-

TABLE I. Spin Hamiltonian parameters of the $^8S_{7/2}$ state of the Gd^{3+} ion paired with different anions in the CaF_2 lattice given in units of 10^{-4} cm^{-1}. These are related to the parameters of Eq. (1) by $b_2^0 = 3B_2^0$, $b_4^m = 60B_4^m$, and $b_6^m = 1260B_6^m$.

Ion pair:	$Gd^{3+}-H^-$	$Gd^{3+}-H^-$	$Gd^{3+}-F^-$	$Gd^{3+}-F^-$ Vinokurov *et al.*
Source:	This paper	This paper	This paper	(Ref. 8)
b_2^0	-1841 ± 2	-1861 ± 2	-1485 ± 1	-1483 ± 3
b_4^0	-23.8 ± 0.2	-23.7 ± 0.2	-23.1 ± 0.1	-23.0 ± 0.7
b_4^4	-114 ± 2	-113 ± 2	-147 ± 1	-146 ± 2
b_6^0	-0.7 ± 0.1	-0.7 ± 0.1	-0.7 ± 0.1	-0.7 ± 0.3
b_6^4	$+4.4 \pm 0.7$	$+4.0 \pm 0.7$	$+5.3 \pm 0.5$	0.0

blance between the physical situations of all these ion pairs.

COMPARISON WITH OPTICAL SPECTRA

The optical spectra corresponding to the transitions between the $^8S_{7/2}$ ground state and the $^6P_{7/2}$ excited state have been measured.[1] Since the crystal-field splitting of the $^6P_{7/2}$ state is much smaller than separations between the J multiplets of the $4f^7$ configuration, the former can be treated by the effective Hamiltonian (1) just as for the ground state $^8S_{7/2}$. The splitting patterns of the $^6P_{7/2}$ state for different tetragonal sites can be approximately related by a simple scale factor,[1] showing that the effect of the $B_2^0O_2^0$ term in (1) dominates over the others. Thus the splitting has been calculated by perturbation theory in the first order, and the parameters $B_2^0(P)$, $B_4^0(P)$, and $B_6^0(P)$ are tabulated in Table II. The symbol (P) is added to distinguish the parameters for the excited $^6P_{7/2}$ state from those for the ground $^8S_{7/2}$ state.

The theory of the crystal-field splitting of the ground $^8S_{7/2}$ state of the Gd^{3+} ion has been presented by Wybourne.[9] If we assume that the entire crystal-field splitting is caused by the interactions within the $4f^7$ configuration, the crystal-field Hamiltonian for C_{4v} symmetry can be written in tensor operators of the type $C_q^{(k)}$ to give[10]

$$V_c = A_0^2C_0^{(2)} + A_0^4C_0^{(4)} + A_4^4(C_{-4}^{(4)} + C_4^{(4)}) + A_0^6C_0^{(6)} + A_4^6(C_{-4}^{(6)} + C_4^{(6)}) \;, \tag{3}$$

with the same A_q^k crystal-field parameters for both the $^6P_{7/2}$ and $^8S_{7/2}$ states. The B_2^0 parameter can be calculated in first order to give

$$B_2^0 = A_0^2\langle {}^8S_{7/2}M \,|\, C_0^{(2)} \,|\, {}^8S_{7/2}M\rangle[3M^2 - J(J+1)]^{-1} \;, \tag{4}$$

where it is understood that $|{}^8S_{7/2}M\rangle$ stands for the ground-state eigenfunction of the total free-ion Hamiltonian, explicitly including spin-orbit interaction. The parameter $B_2^0(P)$ is given by the formula analogous to (4) for the $^6P_{7/2}$ state.

Recently the electrostatic parameters for the $4f^7$ configuration of the Gd^{3+} ions in the CaF_2 lattice were determined from the absorption spectrum down to 1350 Å,[2] so the eigenvectors of the 50×50 matrix of $J = \frac{7}{2}$ intermediate states have been found.[11] Using these results the matrix elements of the $C_0^{(2)}$ operator are

$$\begin{aligned} \langle {}^8S_{7/2}\tfrac{1}{2} \,|\, C_0^{(2)} \,|\, {}^8S_{7/2}\tfrac{1}{2}\rangle &= -0.482 \times 10^{-3} \;, \\ \langle {}^6P_{7/2}\tfrac{1}{2} \,|\, C_0^{(2)} \,|\, {}^6P_{7/2}\tfrac{1}{2}\rangle &= -0.450 \;. \end{aligned} \tag{5}$$

Substituting (5) into (4) and using the tabulated values of B_2^0 parameters for both states, the value of A_0^2 parameters has been found to be + 1910 and + 1950 cm^{-1} for the $^8S_{7/2}$ and $^6P_{7/2}$ states, respectively. Both values are very similar. This suggests that the value of the B_2^0 parameter (which reflects the dominant part of the crystal-field splitting) can be explained by the crystal-field Hamiltonian (2) operating only within the $4f^7$ configuration.

"IONIC" MODEL

There are several contributions to the effective crystal field (3). Besides the crystal field caused by charges outside the Gd^{3+} ion there are covalency and overlap contributions which cannot be overlooked. However, the correlation of the A_0^2 parameters for the ground and the excited states, which are separated in energy by about 30 000 cm^{-1}, encourages us to assume that these contributions to the parameter A_2^0 are small or at least not dominant. In what follows we shall calculate the crystal field by the so-called ionic model. We shall consider the contribution of point monopoles as well as dipoles induced by internal electric field components. Contributions to the potential (3) due to impurity-induced distortions of the lattice will also be incorporated.

To estimate these effects the following simplifications are made. All ions of the undistorted lattice contribute to the potential of cubic symmetry which has no contribution to the A_0^2 parameter. The polarization of cations is neglected. The polarizability of F^- ions is small so that the potential caused by induced dipole moments of F^- ions is calculated in first order, neglecting mutual F^- dipole interactions. The local distortions of the lattice caused by impurity ions are small and their effect is incorporated by introducing effective dipole moments at shifted lattice sites. Dipole moments are then induced only by the extra charge of the Gd^{3+} ion and by the charge and dipole moment of the H^- ion. The dipole moments induced by the Gd^{3+} ion's extra charge produce a potential of cubic symmetry in first order. The main contribution of dipoles induced by the charge and dipole moment of the H^- ion is that of the four F^- ions which are common neighbors of both the Gd^{3+} and H^- ions. Thus, in calculating the parameter A_2^0 we must consider contributions from the single charge and the induced dipole moment of the H^- ion, the induced dipole moments of the four F^- ions, and the effect of shifts of the Gd^{3+}, H^-, and F^- ions from their

TABLE II. Spin Hamiltonian parameters of the $^6P_{7/2}$ state of the Gd^{3+} ion paired with the H^- ion in the CaF_2 lattice given in units of cm^{-1}. These are related to the parameters of Eq. (1) by $b_2^0 = 3B_4^0$, $b_4^0 = 60B_4^0$, and $b_6^0 = 1260B_6^0$.

	$b_2^0(P)$	$b_4^0(P)$	$b_6^0(P)$
Gd^{3+}-H^-	−17.56	0.06	−0.432

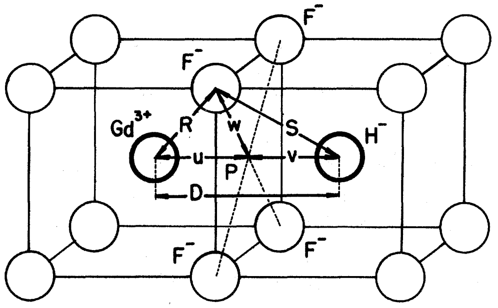

FIG. 1. The arrangement of ions of the gadolinium-hydride ion pair in calcium fluoride. R, S, and D are the distances between ion centers; u, v, and w are the distances between ion centers and the point P, the center of the square formed by the four F^- ions.

regular lattice positions. All these induced dipole moments and ion shifts have to correspond to the C_{4v} symmetry of the Gd^{3+}-H^- pair in the CaF_2 lattice. Using the general formula for the expansion of the dipole moment potential given in the Appendix, the following expression for the parameter A_0^2 can be derived:

$$A_0^2 = er^2 \left[\frac{q}{D^3} - 3\frac{p}{D^4} + \frac{p_r}{A^4} P_3^1\left(\frac{u}{R}\right) - 3\frac{p_z}{A^4} P_3^0\left(\frac{u}{R}\right) + \frac{q_F \delta_r}{A^4} P_3^1\left(\frac{u}{R}\right) - 3\frac{q_F \delta_z}{A^4} P_3^0\left(\frac{u}{R}\right)\right], \tag{6}$$

where

$$p_z = \alpha_F \left[2\frac{p}{S^3} P_2^0\left(\frac{v}{S}\right) - \frac{q}{S^2} P_1^0\left(\frac{v}{S}\right)\right],$$

$$p_r = \alpha_F \left[\frac{p}{S^3} P_2^1\left(\frac{v}{S}\right) - \frac{q}{S^2} P_1^1\left(\frac{v}{S}\right)\right].$$

The meaning of the parameters R, S, D, u, and v, is indicated in Fig. 1. Here e is the electron charge; r is the $4f$ electron radius; q and p are the effective charge and the dipole moment of the H^- ion, respectively; p_r and p_z are the radial and axial components, respectively, of the induced dipole moments of the four F^- ions; α_F is the polarizability of an F^- ion. δ_r and δ_z in (6) are radial and axial shifts, respectively, of the four F^- ions, and the $P_n^m(\xi)$ are Legendre polynomials defined in the Appendix.

There are five independent parameters (for example, R, S, D, δ_r, and δ_z) which define the geometry of the complex. As they are not known, we cannot make any precise calculations. However, the values of these parameters are limited by the elastic forces of the lattice, so that the limits of different contributions to the value of the A_2^0 parameter can be estimated.

Inclusion of the dipole moment p of the H^- ion is important because of the very large polarizability of this ion.[12] The value of the H^- ion polarizability for a small electric field has been both measured and calculated, and it gives for our case the value $p = 7.7ea_0$, where a_0 is the Bohr radius. This value of p is unreasonably large for the hydrogen ion having its nuclear charge equal to $|e|$. However, the dipole moment p causes a shift in the frequency of the H^- local vibrational mode which is discussed elsewhere.[13] The value $p = 1.1ea_0$ has been calculated so as to fit both the measured local-mode frequency of the H^- ion paired with the Gd^{3+} ion and the frequency of the local mode of the H^- ion in the cubic interstitial site. Here, the reduced effective charge of the H^- ion was taken as $q = 0.85e$.

The lattice constant of CaF_2 is equal to 5.46 Å and the polarizability of the F^- ions is taken as $\alpha_F = 1.04$ Å^3. If there are no movements of ions off their regular lattice positions, the calculated value is $A_0^2 = (1060 + 800 - 190)$ cm^{-1}, where the contributions are, respectively, those of the point charge of the H^- ion, the dipole moment of the H^- ion, and the induced dipole moments of F^- ions. Thus, we see that the contribution of the F^- ion's polarization is small and that the point charge and dipole moment of the H^- ion give the decisive contributions.

To estimate the effect of F^- ion shifts we presume that they move radially away from the H^- ion due to their electrostatic repulsion.[14] In that case contributions of the radial and axial shifts to A_2^0 have the same sign, so we obtain the maximum possible value of it. If the value 0.1 Å is accepted for the F^- ion shifts off their regular lattice positions, their contribution to the A_2^0 value is equal to -270 cm^{-1}. Even this is a value which is much smaller than the contribution of the H^- ion itself.

Because of the electrostatic attraction between Gd^{3+} and H^- ions, we can assume that the distance between them is diminished. A change of 0.1 Å in this distance gives a contribution to A_2^0 equal to $+230$ cm^{-1}. This contribution is much smaller than the contribution of the H^- ion in the regular lattice position and it is of the same sign. It should be pointed out that this contribution is nearly canceled by the contribution of the F^- ion shifts.

Notwithstanding the crudeness of the model we can conclude that the calculated value of A_2^0 is of the right sign and of the right order of magnitude. The model can also qualitatively explain the difference between the B_2^0 values for Gd^{3+}-H^- and Gd^{3+}-F^- pairs (Table I). Since the effective charge of the H^- and F^- ions should be almost the same, only a different induced dipole moment can explain the larger value of B_2^0 for Gd^{3+}-H^-. This view is supported by the large polarizability of the H^- ion compared with the F^- ion.[12]

ISOTOPE SHIFT OF ZERO-FIELD SPLITTING

Deuterated calcium fluoride crystals containing gadolinium show ESR lines at magnetic fields slightly different from those in hydrogenated crystals. Crystals heated in a mixed hydrogen-deuterium atmosphere display both sets of lines. Such displacements constitute the ESR-line isotope shift between hydrogen and deuterium.

The interaction between the $4f$ electrons of the Gd^{3+} ion and lattice phonons causes a shift in each electronic level and all lattice modes contribute to this shift. The isotope shift between hydrogen and deuterium is the difference in this shift when deuterium is substituted for hydrogen. It can be assumed that the lattice modes are the same whether hydrogen or deuterium is present since these have local-mode frequencies well above the highest optical frequency of the crystal. Their contribution to an isotope shift is therefore zero. The ESR-line isotope shift can, however, arise through the coupling of the localized-mode vibrations to the electronic states of the gadolinium ion. The widely different zero-point amplitude of vibration for hydrogen and deuterium results in different perturbations of gadolinium electronic states.

The over-all zero-field splitting of the gadolinium ground state is equal to the difference between the energies of the $M_J=\frac{7}{2}$ and $M_J=\frac{1}{2}$ states. Let us define the isotope shift of the zero-field splitting (later referred to as the isotope shift) as the difference between the zero-field splitting of the ground state of the Gd^{3+} ion paired with the H^- ion and that of the Gd^{3+} ion paired with the D^- ion. The measured value of the isotope shift is equal to $-0.024 \pm 0.001\ \text{cm}^{-1}$. Hence the Gd^{3+} ions coupled with D^- ions have a greater ground-state splitting than those coupled with H^- ions.

The electron-phonon interaction between a $4f$ electron of the Gd^{3+} ion and the phonon of the lattice, in the adiabatic approximation, can be written in the general form

$$V_{ev}=\sum_i f_i^\alpha Q_i^\alpha+\sum_{i,j} g_{ij}^{\alpha\beta} Q_i^\alpha Q_j^\beta+\cdots\ , \tag{7}$$

where f_i^α and $g_{ij}^{\alpha\beta}$ are functions of the electron coordinates, and Q_i^α are the phonon normal coordinates which transform according to the αth irreducible representation of the point group of the gadolinium-ion site. As V_{ev} spans the totally symmetric representation of this point group, the electronic coordinate functions, f_i^α and $g_{ij}^{\alpha\beta}$, form bases for the complex-conjugate representations to those of the Q_i^α and $Q_i^\alpha Q_j^\beta$, respectively.

For the electron-phonon interaction involving the localized mode of hydrogen or deuterium ions alone, the phonon normal coordinates are simply X, Y, and Z, the displacements of the light ion from equilibrium. This follows from the small mass of hydrogen and deuterium compared to other ions of the crystal.

The electron local-mode phonon interaction up to terms quadratic in the phonon coordinates has the form (for C_{4v} symmetry)

$$\begin{aligned} V_{ev}&=f_z Z+f_x X+f_y Y+g_{zz} Z^2 \\ &+(g_{xx}+g_{yy})\tfrac{1}{2}(X^2+Y^2)+g_{xz}XZ \\ &+g_{yz}YZ+(g_{xx}-g_{yy})\tfrac{1}{2}(X^2-Y^2)+g_{xy}XY\ , \end{aligned} \tag{8}$$

where the electronic coordinate functions, f_i and g_{ij}, depend on the particular model used for the electron-phonon interaction.

The hydrogen or deuterium ion itself moves in a potential well which can be expanded in a power series of the displacement coordinates XYZ. The potential appropriate to C_{4v} symmetry up to terms of the third degree has the form

$$V=a(X^2+Y^2)+bZ^2+cZ^3+dZ(X^2+Y^2)\ . \tag{9}$$

Since the anharmonic cubic terms in (9) are much smaller than the harmonic ones, the vibrational function of the hydrogen or deuterium local mode can be written in the first order as a product of three one-dimensional harmonic-oscillator wave functions of the X, Y, and Z coordinates.

If the interaction between the gadolinium electronic levels and the hydrogen or deuterium local mode and the anharmonic terms in (9) is neglected, the wave functions for the combined system (vibronic wave functions) take the product form

$$\psi_{in}=\varphi_i\psi_n\ , \tag{10}$$

where φ_i and ψ_n are electronic wave functions and vibrational wave functions, respectively. Then the small electron-phonon interaction terms (8) and anharmonic terms in (9) can be taken as perturbations on the vibronic functions (10). Taking the ${}^8S_{7/2}$ electronic wave functions, combined with all the vibrational wave functions, as the basis set, the energy corrections calculated up to second order are as follows:

$$\begin{aligned} \Delta E_M=&-\frac{\beta_z^2}{\hbar w_z}\,|\langle M|f_z|M\rangle|^2-\sum_{M'\neq M}\frac{\beta_x^2}{\hbar w_x}\left(1+\frac{E_M}{\hbar\omega_x}\right)^{-1} \\ &\times[\,|\langle M|f_x|M'\rangle|^2+|\langle M|f_y|M'\rangle|^2] \\ &-\frac{6\beta_z^4}{\hbar w_z}c\,\langle M|f_z|M\rangle-\frac{2\beta_z^4}{\hbar w_z}d\langle M|f_z|M\rangle \\ &+\beta_z^2\langle M|g_{zz}|M\rangle+\beta_x^2\,\langle M|g_{xx}+g_{yy}|M\rangle\ , \end{aligned} \tag{11}$$

where $\beta_i^2=\hbar/2mw_i$, m is the hydrogen or deuterium mass, w_z and w_x are the frequencies of the longitudinal and the transverse hydrogen or deuterium vibrations, respectively, and the matrix elements are understood to be calculated between the ground-state wave functions which diagonalize the total Hamiltonian of Gd^{3+} in the crystal field of CaF_2.

The isotope shift is given by the difference in the energy corrections (11) when going from hydrogen to deuterium. (i) The first term in (11) does not contribute to the isotope shift since the term $\beta_z^2/\hbar w_z$ (the force constant) is the same for hydrogen and deuterium. The second term contributes to the isotope shift but it is reduced by the factor $E/\hbar w$, where E is the zero-field splitting of the Gd^{3+} ground state. This factor is about 2×10^{-3}, so that the contribution of the second term to the isotope shift is negligible when compared with contributions of the other terms in (11). (ii) The third and fourth terms in (11) caused by the second-order perturbation contribute to the isotope shift and they depend on the cubic anharmonic constants c and d of the local-mode vibration. Their contributions will be referred to as the anharmonic contributions to the isotope shift. (iii) The fifth and sixth terms in (11) are caused by the second-degree terms of the electron-phonon interaction in first-order perturbation. To distinguish them from (ii) we shall refer to them as the harmonic contributions to the isotope shift.

The electronic function f_z can be expanded as a series of tensor operators $C_q^{(k)}$ to give

$$f_z = \sum_{n=2,4,6} \alpha_0^{(n)} C_0^{(n)} + \alpha_4^{(4)} (C_{-4}^{(4)} + C_{+4}^{(4)}) + \alpha_4^{(6)} (C_{-4}^{(6)} + C_{+4}^{(6)}) , \tag{12}$$

and expressions of the same form can be written for the functions g_{zz} and $g_{xx}+g_{yy}$, with the constants $\beta_m^{(n)}$ and $\gamma_m^{(n)}$, respectively, in place of the constants $\alpha_m^{(n)}$ in (12). Values of these constants depend on the particular model chosen for the calculation of the electron local-mode phonon interaction. If the interaction between the Gd^{3+} ion and the H^- or D^- ion only is taken into account, the lattice ions being omitted, the constants $\alpha_4^{(4)}$ and $\alpha_4^{(6)}$ in (12) (and the corresponding β and γ constants) are equal to zero.

The cubic anharmonic constants c and d have been estimated from the infrared local-mode spectra of the Ce^{3+}-H^- pair and from the ionic model of the local mode described elsewhere.[13] The values so obtained are $c = +6\times 10^{11}$ erg/cm^3 and $d = +6.5 \times 10^{11}$ erg/cm^3.

The values of the $\alpha_0^{(n)}$, $\beta_0^{(n)}$, and $\gamma_0^{(n)}$ coefficients can be calculated using the ionic model introduced in Sec. III. It is expected that the direct interactions between the $4f$ electrons of the Gd^{3+} ion and the point charge and the dipole moment of the H^- ion will give the principal contributions to the isotope shift. The values of the coefficients $\alpha_0^{(n)}$, $\beta_0^{(n)}$, and $\gamma_0^{(n)}$ for these interactions are given in the Appendix, and they have been used, together with c and d given above, to calculate both the anharmonic and harmonic contributions to the isotope shift of the zero-field splitting (Table III). The harmonic contribution due to the point charge alone of the H^- ion is the only one giving the same sign as the experiment.[15] However, this contribution is very small. In fact, in this case the two functions g_{zz} and $g_{xx}+g_{yy}$ have the same value but opposite sign, so their contributions nearly cancel. Complete cancellation does not occur because of the difference in the radial and axial frequencies of the H^- local mode. Due to the small anisotropy of these frequencies, the resulting contribution to the isotope shift is also very small.

The harmonic contribution to the isotope shift caused by the dipole moment of the H^- ion is bigger than that caused by its point charge. This is because the dipole moment, being pointed to the center of the Gd^{3+} ion, provided a partial rotation simultaneously with the radial vibration of the H^- ion. This partial rotation disturbs the equality of the g_{zz} and $g_{xx}+g_{yy}$ functions which holds otherwise. However, as can be seen from Table III, the sign of this contribution is not in accordance with experiment.

The anharmonic contribution to the isotope shift caused by both the point charge and dipole moment of the H^- ion are of the greatest absolute value but of the wrong sign. Nevertheless, even the absolute value of all contributions added together is about 4 times smaller than the experimental value.

A further attempt has been made to explain the isotope shift within the ionic model. Besides the direct interaction between the H^- ion and the $4f$ electrons, the dynamic polarization of the four fluorine ions which are mutual neighbors of the Gd^{3+} ion and the H^- ion has been taken into account. The coefficients $\alpha_0^{(2)}$, $\beta_0^{(2)}$, and $\gamma_0^{(2)}$ in (12) caused by this polarization are given in the Appendix. Their contributions to the isotope shift are given in the Table III for the case where all ions are in the regular sites of the lattice. (It has been shown that

TABLE III. The calculated contributions to the isotope shift of the zero-field splitting (energy units in 10^{-2} cm^{-1}). Anharmonic (AS) and harmonic (HS) shift contributions discussed in the text are tabulated for the direct interactions with the point charge and the dipole moment of the H^- ion and for the interaction caused by the dynamic polarization of four F^- ions. The net calculated value is $+0.600 \times 10^{-2}$ cm^{-1}, compared with the experimental value of 2.4×10^{-2} cm^{-1}.

Contribution due to:	AS	HS
Charge of H^-	+0.360	−0.038
Dipole of H^-	+0.306	+0.080
Polarization of $4F^-$	−0.031	−0.077

0.1-Å shifts of these ions give no substantial change for the calculated values.) The common feature of these contributions is that they are all of the right sign. The value of the harmonic contribution is larger than the value of the anharmonic contribution. However, the absolute values of both these contributions are even smaller than the absolute values of contributions caused by the direct interactions between $4f$ electrons and the H^- ion.

CONCLUSION

An attempt has been made to interpret the measured tetragonal crystal-field splittings of the $^8S_{7/2}$ and $^6P_{7/2}$ states of the Gd^{3+} ion paired with the H^- ion, using the ionic model and interactions between levels of the $4f^7$ configuration. It was shown that both the order of magnitude and the sign of the crystal-field splitting can be explained satisfactorily. No undue optimism about the quantitative accuracy of these results is implied but they are an improvement on the result achieved from an ionic treatment of a Gd^{3+} ion impurity in ethyl sulphate, where a wrong sign was obtained. It is believed that the reason for this difference lies in the relative importance of covalency effects in the two cases. The crystal-field potential in the case of Gd^{3+} in CaF_2 is mainly caused by the H^- ion in the next-nearest-neighbor interstitial site, whereas in ethyl sulphate it is due to nearest-neighbor ligand ions. Overlap between the Gd^{3+} and H^- orbitals is, therefore, less important than overlap between the Gd^{3+} and the ligand ion orbitals in ethyl sulphate.

The isotope shift between the zero-field splitting of the Gd^{3+}-H^- pair and the Gd^{3+}-D^- pair is assumed to be caused by the electron-phonon interaction between the $4f$ electrons of the Gd^{3+} ion and the local mode of the H^- or D^- ion. It was pointed out that there are two types of isotope-shift contribution, called the harmonic and the anharmonic contribution, both being of comparable importance. However, the ionic model gives a result which is too small in its absolute value and of the wrong sign if compared with the experimental result. Considering the relatively good result achieved for the zero-field splitting, two possible additional contributions to the isotope shift can be suggested. First, the inclusion of the overlap of the H^- ion orbitals with those of the Gd^{3+} ion may be more important for the isotope shift than for the zero-field splitting. In fact the isotope shift would depend on the derivative of this overlap and not on its value, as is the case for the zero-field splitting. Second, the electron-phonon interaction between the hydrogen-ion electrons and its local mode can slightly change the polarization of the ground-state wave function, so that the effective dipole moments of hydrogen and deuterium are slightly different and give different terms in the electron-phonon interaction for the two cases. Analysis of the isotope shift of a $5d$ electron level of the Ce^{3+}-H^- pair[13] gives very similar results to the ones achieved here. Since there is a large difference in the ionic radii of the $5d$ and $4f$ shells, we would suggest that the second point is more likely than the first to explain the discrepancies.

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APPENDIX

For the calculation of the crystal field of point charges, an expansion in terms of spherical harmonics of two systems of coordinates is commonly used. If the crystal field caused by dipole moments, or the coefficients of the electron-phonon interaction are to be calculated, derivatives of the potential function are needed. If Cartesian systems of coordinates are used, simple relations between derivatives with respect to coordinates of the first or the second coordinate system hold. It is then convenient to expand the potential function in terms of three-dimensional functions, the so-called solid harmonics of degree n and order m,

$$T^m_{nx} = r^n P^m_n(\cos\theta)\cos m\varphi, \qquad T^m_{ny} = r^n P^m_n(\cos\theta)\sin m\varphi\ , \tag{A1}$$

for $n, m = 0, 1, 2, 3, \cdots$ and $m \leq n$, where r, θ, and φ are spherical coordinates and $P^m_n(\xi)$ are Legendre polynomials

$$P^m_n(\xi) = (-1)^n \frac{(1-\xi^2)^{m/2}}{2^n n!} \frac{d^{n+m}}{d\xi^{n+m}} (\xi^2 - 1)^n. \tag{A2}$$

The solid harmonics (A1) can be easily differentiated with respect to the Cartesian coordinates $x = r \times \sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$, and $z = r\cos\theta$ by using the following recurrence formulas.

For differentiation with respect to x and y for $m > 0$:

$$2\frac{\partial}{\partial x} T^m_{n,x} = -(n+m)(n+m-1)T^{m-1}_{n-1,x} + T^{m+1}_{n-1,x}\ ,$$

$$2\frac{\partial}{\partial x}T^m_{n,y}=-(n+m)(n+m-1)T^{m-1}_{n-1,x,}+T^{m+1}_{n-1,y},$$

$$2\frac{\partial}{\partial y}T^m_{n,x}=(n+m)(n+m-1)T^{m-1}_{n-1,y}+T^{m+1}_{n-1,y},$$

$$2\frac{\partial}{\partial y}T^m_{n,y}=-(n+m)(n+m-1)T^{m-1}_{n-1,x}-T^{m+1}_{n-1,x},$$

and for $m=0$:

$$\frac{\partial}{\partial x}T^0_n=T^1_{n-1,x},\qquad \frac{\partial}{\partial y}T^0_n=T^1_{n-1,y},\tag{A3}$$

and for differentiation with respect to z, for $m\geqslant 0$:

$$\frac{\partial}{\partial z}T^m_{n,x}=(n+m)T^m_{n-1,x}\ ,\qquad \frac{\partial}{\partial z}T^m_{n,y}=(n+m)T^m_{n-1,y}\ .$$

Here $n=0,\ 1,\ 2,\ \ldots,\ m=0,\ 1,\ 2,\ \ldots,n$, and $T^m_{ni}=0$ for $m>n$. Moreover, the quantity $T^0_n=T^0_{n,x}$ has been introduced, and it should be understood that $T^0_{n,y}=0$, as implied by (A1).

The Coulomb potential at $\vec{r}$ of a unit point charge at $\vec{R}$ can be expanded in terms of the solid harmonics (A1), for $|\vec{R}|>|\vec{r}|$,

$$\frac{1}{|\vec{R}-\vec{r}|}=\sum M^m_n R^{-(2n+1)}[T^m_{nx}(\vec{R})T^m_{nx}(\vec{r})+T^m_{ny}(\vec{R})T^m_{ny}(\vec{r})]\ ,\tag{A4}$$

where

$$M^m_n=2\frac{(n-m)!}{(n+m)!}\quad\text{for}\quad m\neq 0$$

and

$$M^0_n=1\qquad\text{for}\quad m=0\ .$$

This relation (A4) can be used for the derivation of the dipole moment potential. The dipole moment potential is equal to the scalar product of the dipole moment vector p and the gradient of the potential function (A4). Using the relations (A3) applied to (A4), the expansion of the dipole moment potential in terms of solid harmonics can be derived as follows:

$$p\cdot\mathrm{grad}\frac{1}{|\vec{R}-\vec{r}|}=p_x\frac{\partial}{\partial x}\frac{1}{|\vec{R}-\vec{r}|}+p_y\frac{\partial}{\partial y}\frac{1}{|\vec{R}-\vec{r}|}+p_z\frac{\partial}{\partial z}\frac{1}{|\vec{R}-\vec{r}|}\ ,$$

where for $s=x,\ y$,

$$\begin{aligned}\frac{\partial}{\partial s}\frac{1}{|\vec{R}-\vec{r}|}&=\sum R^{-(2n+3)}T^1_{n+1,s}(\vec{R})T^0_n(\vec{r})-\sum R^{-(2n+3)}T^0_{n+1}(\vec{R})T^1_{n,s}(\vec{r})\\&+\sum_n\sum_{m>0}R^{-(2n+3)}\Big\{(n+2)(m+3)\frac{(n+m)!}{(n+m+2)!}[T^{m+1}_{n+1,x}(\vec{R})T^m_{n,x}(\vec{r})+T^{m+1}_{n+1,y}(\vec{R})T^m_{n,y}(\vec{r})]\\&-\frac{(n-m+2)!}{(n+m)!}[T^{m-1}_{n+1,x}(\vec{R})T^m_{n,x}(\vec{r})+T^{m-1}_{n+1,y}(\vec{R})T^m_{n,y}(\vec{r})]\Big\}\end{aligned}\tag{A5}$$

and

$$\begin{aligned}\frac{\partial}{\partial z}\frac{1}{|\vec{R}-\vec{r}|}&=-\sum_n(n+1)R^{-(2n+3)}T^0_{n+1}(\vec{R})T^0_n(\vec{r})\\&-2\sum_n\sum_{m>0}\frac{(n-m+1)!}{(n+m)!}R^{-(2n+3)}[T^m_{n+1,x}(\vec{R})T^m_{n,x}(\vec{r})+T^m_{n+1,y}(\vec{R})T^m_{n+1,y}(\vec{r})]\ .\end{aligned}$$

The electronic functions f_i and g_{ij} in the expression for the electron-phonon interaction (8) can be obtained by differentiations of the interaction energy between the $4f$ electron of Gd^{3+} and the hydride ion. For the ionic model they can be expanded in terms of the solid harmonics using relations (A3). Since the tensor operators $C^{(n)}_m$ are related to the solid harmonics (1) as follows:

$$C^{(n)}_{\pm m}=r^{-n}\left(\frac{(n-m)!}{(n+m)!}\right)^{1/2}(T^m_{n,x}\pm iT^m_{n,y})\ ,\tag{A6}$$

expansions of f_i and g_{ij} in the $C^{(k)}_q$ can be easily found. In this way the constants $\alpha^{(n)}_0$ in (12) (and the corresponding β and γ constants) have been calculated for the interaction between the point charge q of the H^- ion and the $4f$ electron as follows:

$$\begin{aligned}\alpha^{(n)}_0&=-(eq/D^{n+2})(n+1)r^n\ ,\\\beta^{(n)}_0&=-\gamma^{(n)}_0=(eq/D^{n+3})\tfrac{1}{2}(n+1)(n+2)r^n\ .\end{aligned}\tag{A7}$$

For the interaction between the dipole moment p of the H^- ion and the $4f$ electron they are given as follows:

$$\begin{aligned}\alpha^{(n)}_0&=(ep/D^{n+3})(n+1)(n+2)r^n,\\\beta^{(n)}_0&=-(ep/D^{n+4})\tfrac{1}{2}(n+1)(n+2)(n+3)r^n\ ,\\\gamma^{(n)}_0&=-(ep/D^{n+4})\tfrac{1}{2}(n+1)[(n+1)(n+2)+2]r^n\ .\end{aligned}\tag{A8}$$

For the indirect interaction calculated as the potential energy of the 4f electron in the field of dipoles of four fluorines dynamically polarized by the moving point charge of the H$^-$ ion the second-degree terms are as follows:

$$\alpha_0^{(2)} = \frac{\alpha_F eq}{2R^4S^3}\, r^2 \left\{ \frac{4v}{S^2}\left[4w P_3^1\left(\frac{u}{R}\right) + 3vP_3^0\left(\frac{u}{S}\right)\right] - 24P_3^0\left(\frac{u}{R}\right)\right\},$$

$$\beta_0^{(2)} = -\frac{2\alpha_F eq}{R^4S^5}\, r^2 \left\{\left(\frac{5v^2}{S^2} - 1\right)\left[4wP_3^1\left(\frac{w}{R}\right) + 3vP_3^0\left(\frac{w}{R}\right)\right] - 24vP_3^0\left(\frac{u}{R}\right)\right\}, \tag{A9}$$

$$\gamma_0^{(2)} = \frac{\alpha_F eq}{R^4S^5}\, r^2 \left[8w\left(5\frac{w^2}{S^2} - 3\right) P_3^1\left(\frac{u}{R}\right) + 3v\left(10\frac{w^2}{S^2} - 1\right) P_3^0\left(\frac{u}{R}\right)\right].$$

The meaning of the parameters R, S, D, u, v, and w is indicated in Fig. 1.

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Hyperfine, Superhyperfine, and Quadrupole Interactions of Gd^{3+} in YPO$_4$

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The electron-paramagnetic-resonance spectrum of Gd^{3+} in YPO$_4$ shows a superhyperfine structure from two nearest-neighbor phosphorus nuclei when observed with $\vec{H}$ parallel to the crystal c axis. The spectrum for $\vec{H}$ perpendicular to the c axis is unusual because of quadrupole interactions in Gd^{155} and Gd^{157} which are larger than the hyperfine interaction in these ions. The measured Gd^{3+}-P interaction parameter $|T_\parallel| = 1.02$ G fits well a dipole-dipole interaction model. The hyperfine parameters are $A^{155} = -4.7$ G and $A^{157} = -6.1$ G. The quadrupole-interaction parameters are $|Q^{155}| = 18.1$ G and $|Q^{157}| = 19.3$ G. From these the ratio of the nuclear quadrupole moments of Gd^{155} and Gd^{157} is obtained as 0.94 ± 0.01. This result is discussed in the light of quadrupole moments previously measured by optical and nuclear methods.

I. INTRODUCTION

Paramagnetic resonance of Gd^{3+} in YPO$_4$ has been recently observed by several authors.[1-3] Variable-frequency zero-field EPR[1,2] and conventional EPR[3] were used to determine the magnitude and sign[3] of the crystal-field parameters b_n^m. These parameters[4] describe the splitting of the $^8S_{7/2}$ ground