

Submillimeter resonance spectroscopy of Ho^{3+} in lithium yttrium fluoride

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The three lowest energy levels of Ho^{3+} in LiYF_4 are determined by submillimeter EPR spectroscopy. The ground state is a $\Gamma_{3,4}$ doublet. The next excited levels are two Γ_2 singlets at 6.8 and 23.8 cm^{-1} . The g_{\parallel} value for the $\Gamma_{3,4}$ doublet is 13.3 ± 0.1 . The couplings between the two Γ_2 singlets, and between the $\Gamma_{3,4}$ doublet and the first Γ_2 singlet are determined.

I. INTRODUCTION

The recent development of lithium yttrium fluoride (LiYF_4) as a laser host material,^{1,2} and the observation of dipolar coupling in the Ising ferromagnet LiTbF_4 ,³⁻⁵ has renewed the interest in materials with the scheelite structure. In this connection, a precise determination of the energy levels and wave functions of the rare-earth ions in this structure is important.

In this paper we report the results of electron-paramagnetic-resonance experiments (EPR) at very high frequencies on Ho^{3+} in LiYF_4 . The experiments were performed in a range of frequencies $70 < \nu < 600$ GHz ($2.3 < \sigma < 20$ cm^{-1}), much higher than in conventional experimental setups. Classical EPR experiments allow in most cases only the probing of transitions within doublets. The use of very high frequencies, on the other hand, allows the determination of several of the lowest levels of the rare-earth ions, through the observation of singlet-singlet, singlet-doublet, etc., transitions. On the other hand, the use of large magnetic fields, up to 5.56 T, is most important because it yields precise information on the wave functions of these levels through the magnetic field dependence of the observed transitions. The measurements therefore provide a test for crystal-field calculations.

Some EPR experiments in the far infrared using molecular lasers have been reported.⁶ The technique used in this work bridges the gap between these laser experiments and the standard EPR experiments and extends the overlap between EPR and optical Zeeman spectroscopy. Furthermore, whereas EPR spectra of Nd^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} in LiYF_4 have been obtained by Sattler and

Nemarich,⁷ and of Tb^{3+} by Laursen and Holmes,⁸ no such spectra have been reported to our knowledge for Ho^{3+} .

II. EXPERIMENTAL SETUP AND SAMPLES

The microwave setup is a simple transmission system. At each frequency, the power transmitted through the sample mounted on a rotating sample holder is measured by a carbon bolometer as a function of the steady magnetic field. Using a small amplitude modulation of the magnetic field, the derivative of the transmitted signal is obtained. The microwave sources consist of a klystron emitting in the 70-GHz range, and eight carcinotrons made by Thomson-CSF which cover the frequency range $77 < \nu < 600$ GHz. The magnetic field produced by a superconducting magnet can be swept up to 5.56 T. The experiments are performed at liquid-helium temperatures. The sample holder is shown on Fig. 1. From the sources to the sample the microwave propagates along oversized wave guides. It is directed on to the front surface of the sample, a crystallographic plane, through a coupling hole. No cavity is used. The bolometer consists of an Allen-Bradley resistor thinned down to about 0.2 mm. The modulation coil is driven by an audio amplifier at a frequency of 87 Hz.

The sample holder sits in a Dewar which communicates with the Dewar of the superconducting coil through a capillary and a needle valve operated from the outside. This Dewar fits inside the core of the superconducting coil. Temperatures lower than 4.2 K are obtained by closing the needle valve and pumping on the helium bath of the inner Dewar.

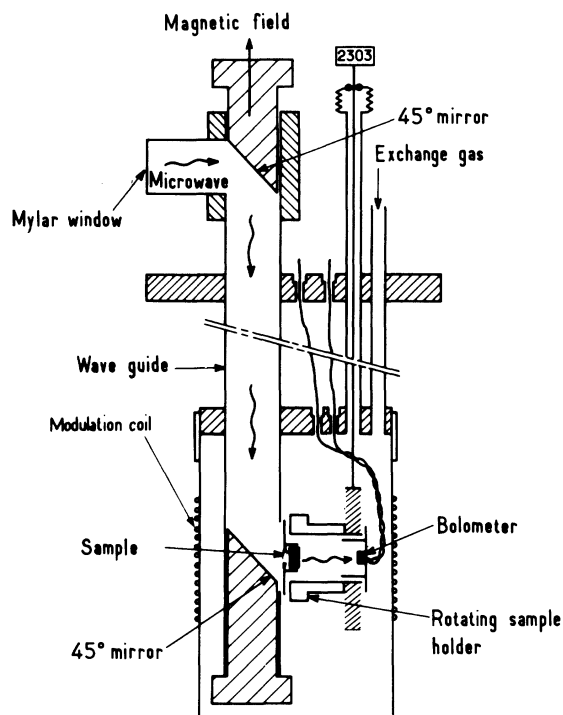


FIG. 1. Sample holder.

The bottom part of the sample-holder is located in a chamber, sealed with Wood's metal, which can be evacuated or filled with helium used as exchange gas.

All samples used in this study were prepared at MIT.⁹ Typical crystals had 0.5% or 2% holmium content. They were cut in the form of parallelepipeds with $3 \times 3 \times 2$ mm³ dimensions. The faces of the samples are crystallographic planes and are mounted on the sample holder, so as to be parallel to the steady magnetic field \vec{B} . LiYF_4 crystallizes in the scheelite structure and belongs to the tetragonal space group C_{4h} . The Y^{3+} ions are at sites of S_4 symmetry. Trivalent rare-earth ions enter the lattice substitutionally for Y^{3+} without charge compensation and with negligible distortion. This is confirmed by the experimental results described below.

III. RESULTS AND INTERPRETATION

At a given frequency we observe in general several groups of eight resonance lines. Each group of lines is due to the 100% abundant isotope ^{165}Ho of holmium of nuclear spin $I = \frac{7}{2}$. The spacing between the hyperfine resonance lines is 479 ± 7 G along c . The angular dependences of all the observed resonance spectra are compatible with the S_4 symmetry, indicating that Ho^{3+} enters LiYF_4 substitutionally for Y^{3+} . The extreme positions of

the spectra are observed along the a and c axes, which suggests that lattice distortion around the impurity is negligible.

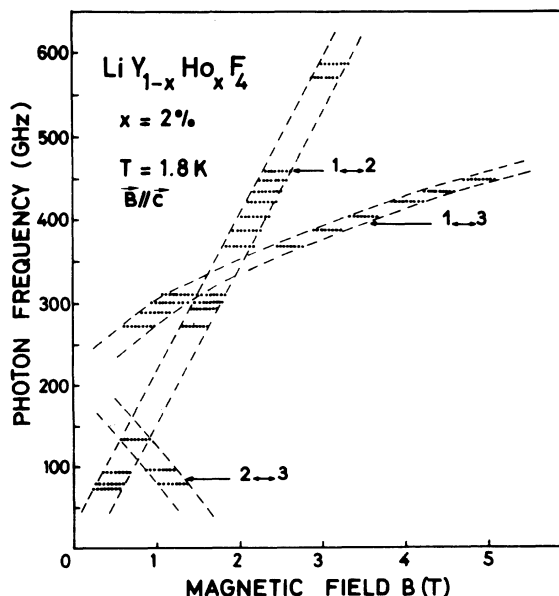
Figures 2 and 3 show the frequency dependence of the observed resonances as a function of the magnetic field \vec{B} , respectively, along the c and a axes. On these figures, note that one group of lines extrapolates to zero frequency at zero magnetic field. This is characteristic of transitions between the levels of a doublet. Two groups of lines extrapolate at 205 GHz (6.8 cm^{-1}), and consequently are due to transitions between a doublet and a singlet, 6.8 cm^{-1} apart. For $\vec{B} \parallel \vec{a}$, one group of lines extrapolates at about 510 GHz (17 cm^{-1}) and therefore corresponds to transitions between two singlets 17 cm^{-1} apart.

These observations can be understood as follows: In a crystal field of S_4 symmetry, the $(2J+1)$ -fold degenerate ground term 5I_8 of the non-Kramers $\text{Ho}^{3+}(4f^{10})$ ion is split into 13 levels (nine singlets and four doublets),

$$^5I_8 - 5\Gamma_1 + 4\Gamma_2 + 4\Gamma_{3,4}.$$

The $\Gamma_{3,4}$ doublets correspond to pairs of singlet representations which are degenerate with respect to time reversal. Optical spectra by Jenssen *et al.*¹⁰ show that the splitting of the 5I_8 ground term is of the order of 300 cm^{-1} . However, the ordering of the different levels is not determined.

Wortman and Sanders¹¹ have shown that for Ho^{3+} in CaWO_4 , the lowest level is a $\Gamma_{3,4}$ doublet and that the first two excited levels are Γ_2 singlets at approximately 9 and 24 cm^{-1} , respectively. In

FIG. 2. Frequency versus magnetic field plot of the resonance lines observed for $\vec{B} \parallel \vec{c}$.

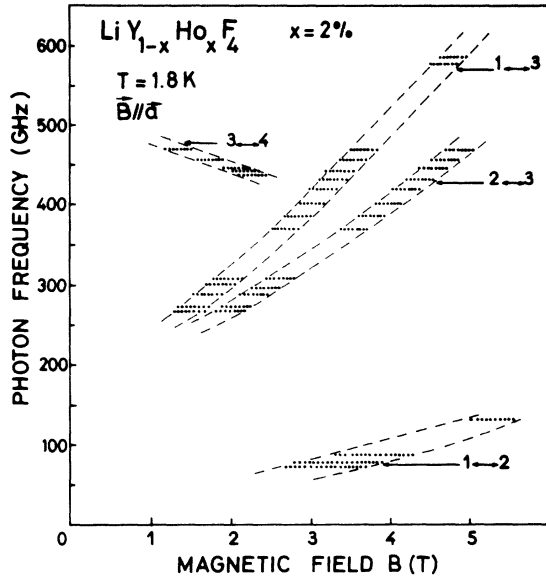


FIG. 3. Frequency versus magnetic field plot of the resonance lines observed for $\vec{B} \parallel \vec{a}$.

very much the same way the only scheme for the energy levels consistent with our observations and depopulation factors at 1.8 K, consists of a ground state $\Gamma_{3,4}$ doublet with two excited $\Gamma_2^{(1)}$ and $\Gamma_2^{(2)}$ singlets at 6.8 and 23.8 cm^{-1} .

The magnetic field dependence of these levels can be obtained from the Zeeman Hamiltonian

$$\mathcal{H}_Z = g_J \mu_B \vec{B} \cdot \vec{J}$$

and from the knowledge of the wave functions of the levels. The Landé factor g_J for the 5I_8 subspace is equal to $\frac{5}{4}$. The general structure of the wave functions is given by group theory. Neglecting the mixing of different J levels for the 5I_8 ground term, and choosing the quantization z axis along the c axis, they read

$$\begin{aligned} |\Gamma_{3,4}\rangle &= \alpha_1 |\pm 7\rangle + \alpha_2 |\pm 3\rangle + \alpha_3 |\mp 1\rangle + \alpha_4 |\mp 5\rangle \\ |\Gamma_2^{(1)}\rangle &= \beta_i (|6\rangle - e^{j\phi_i} |-6\rangle) + \gamma_i (|2\rangle - e^{j\chi_i} |-2\rangle). \end{aligned}$$

The g_{\parallel} value for the $\Gamma_{3,4}$ doublet is given by the diagonal matrix element of the Hamiltonian \mathcal{H}_Z within the $\Gamma_{3,4}$ levels. Experimentally, we find $g_{\parallel} = 13.3 \pm 0.1$. This large value suggests that the states $|\Gamma_{3,4}\rangle$ read to a good approximation

$$|\Gamma_{3,4}\rangle = \alpha_1 |\pm 7\rangle + \alpha_2 |\pm 3\rangle.$$

In a spin- $\frac{1}{2}$ formalism this yields

$$g_{\parallel} = 2g_J (4|\alpha_1|^2 + 3),$$

from which we find $|\alpha_1| = 0.76$ and $|\alpha_2| = 0.65$.

The study of the $\Gamma_{3,4} \rightarrow \Gamma_2^{(1)}$ transitions, noted as $1 \rightarrow 3$ and $2 \rightarrow 3$ in Fig. 2, gives the magnetic

field dependence of the $\Gamma_2^{(1)}$ level. In this case, where $\vec{B} \parallel \vec{z} \parallel \vec{c}$, this dependence is governed by the matrix element:

$$\langle \Gamma_2^{(2)} | \mathcal{H}_Z | \Gamma_2^{(1)} \rangle = g_J \mu_B B \langle \Gamma_2^{(2)} | J_z | \Gamma_2^{(1)} \rangle.$$

The coupling to the other Γ_2 levels which are at much higher energies, of the order of 300 cm^{-1} , is neglected. The best fit to the experimental data is obtained for the value 4.6 ± 0.1 of $|\langle \Gamma_2^{(1)} | J_z | \Gamma_2^{(2)} \rangle|$. For $\vec{B} \parallel \vec{a}$, the Zeeman Hamiltonian couples the $\Gamma_{3,4}$ doublets to the Γ_1 and Γ_2 singlets. The slight Zeeman splitting of the ground-state $\Gamma_{3,4}$ doublet, corresponding to transitions $1 \rightarrow 2$ on Fig. 3, results mainly from the coupling of each level of this doublet to the first excited $\Gamma_2^{(1)}$ singlet. It therefore gives the matrix element

$$|\langle \Gamma_2^{(1)} | J_{x,y} | \Gamma_{3,4} \rangle|.$$

We obtain the value 2.3 ± 0.1 . However, for a more precise fit to the experiment one has to take into account the coupling to the next excited state, $\Gamma_2^{(2)}$ at 23.8 cm^{-1} .

The magnetic field dependence of the three lowest energy levels is plotted on Fig. 4 with the values of the matrix elements determined above. All the features of the frequency dependences shown on Figs. 2 and 3 follow immediately from Fig. 4.

Our results can be compared to calculations of the energy levels and wave functions of Ho^{3+} in LiYF_4 by Karayianis and Wortman.¹² They have diagonalized the effective Hamiltonian

$$\mathcal{H} = \sum_n \lambda_n (\vec{L} \cdot \vec{S})^n + \sum_{km} B_{km}^+ C_{km}$$

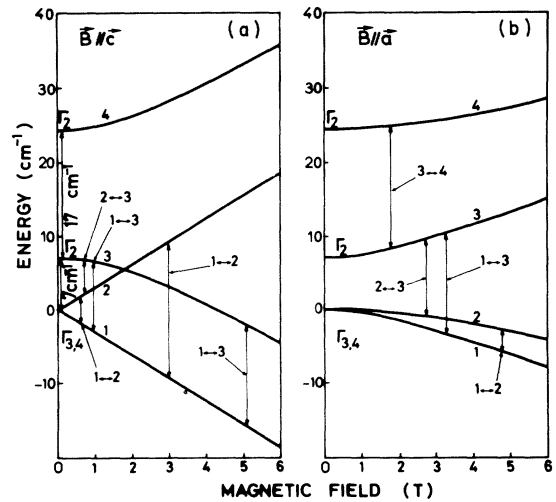


FIG. 4. Theoretical magnetic field dependence of the $\Gamma_{3,4}$, and Γ_2 levels for (a) $\vec{B} \parallel \vec{c}$; (b) $\vec{B} \parallel \vec{a}$.

where the first operator is an effective free-ion Hamiltonian, and the second the crystal-field Hamiltonian. Using values of the parameters which are estimates based on the analysis of Ho^{3+} in CaWO_4 for the λ_n , and of Er^{3+} in LiYF_4 for the B_{km} , they find that the ground state is of $\Gamma_{3,4}$ symmetry, and that the first excited states are Γ_2 singlets at 9 and 24 cm^{-1} . They give $g_{\parallel} = 13.69$, $|\alpha_1| = 0.79$, and $|\alpha_2| = 0.62$. From their wave functions we obtained the matrix elements

$$|\langle \Gamma_2^{(2)} | J_z | \Gamma_2^{(1)} \rangle| = 4.68$$

and

$$|\langle \Gamma_2^{(1)} | J_{x,y} | \Gamma_{3,4} \rangle| = 2.30.$$

These values are in good agreement with the experimental ones.

IV. CONCLUSIONS

EPR experiments in a large range of millimeter and submillimeter wavelengths give novel and precise information on the lowest levels of the Ho^{3+} ion in the scheelite structure, through the deter-

mination of diagonal and nondiagonal matrix elements of the $\Gamma_{3,4} \leftrightarrow \Gamma_{3,4}$, $\Gamma_{3,4} \leftrightarrow \Gamma_2^{(1)}$, and $\Gamma_2^{(1)} \leftrightarrow \Gamma_2^{(2)}$ transitions. The g_{\parallel} value for the $\Gamma_{3,4}$ doublet is determined for the first time in LiYF_4 . This should help in the analysis of the optical spectrum of Ho^{3+} in this material. We believe that the technique should prove very useful for all rare-earth ions, Kramers, and non-Kramers. It provides precise information for crystal-field theorists.

We wish to emphasize that the work reported here relies entirely on the use of an almost continuous range of submillimeter waves and of large magnetic fields at the same time. Studies of Ho^{3+} made at usual microwave or far-infrared frequencies cannot lead to a determination of the couplings between the lowest levels of Ho^{3+} , because not enough transitions would be observed.

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