Paramagnetic and Optical Spectra of Ytterbium in the Cubic Field of Calcium Fluoride*

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The paramagnetic resonance spectrum of Yb^{3+} in CaF_2 was observed at 20°K and 3 cm wavelength. The spectrum is described by a cubic spin Hamiltonian $\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{S}\cdot\mathbf{I}$ with $g=3.426\pm0.001$, $S=\frac{1}{2}$, $A^{171}=(886.5\pm1.5)\times10^{-4}$ cm^{-1}, $A^{173}=(243.2\pm0.4)\times10^{-4}$ cm^{-1}, $I^{171}=\frac{1}{2}$, $I^{173}=\frac{5}{2}$. The ratio of magnetic moments is $\mu^{173}/\mu^{171}=1.374_9\pm0.005$. The optical spectrum shows lines of 9774A, 9770A, 9763 A, and more diffuse and unresolved bands at 9080 and 12730 A. The paramagnetic spectrum is explained as arising from the Γ_7 doublet. The other levels are removed by at least a few cm^{-1} leading to an isotropic g value of 3Λ or 24/7 for the lowest Γ_7 level.

INTRODUCTION

THE spectra of trivalent cerium and ytterbium are complementary, and are the simplest configuration in the rare earth group. We have recently investigated the paramagnetic and optical spectrum of Ce^{3+} in a single crystal of CaF_2.[1] We here present data of these spectra for ytterbium in CaF_2. This ion can with ease be substituted for Ca^{2+} and the point symmetry of a cubic field is preserved. These spectra indicate that the cubic field parameters in the rare earth ion are relatively small, and that the initial splitting is only a few cm^{-1}. The substance is probably a very good material for a three-level submillimeter maser.

THEORY AND EXPERIMENTAL RESULTS

The ground state of Yb^{3+} is $^2F_{7/2}$. The next level is $^2F_{5/2}$ and is removed by about 10300 cm^{-1}. The ground state can therefore be considered to be spanned by $J=7/2$ manifold. This level splits up in a general cubic field to sixth order into a doublet Γ_7 at $-18c-12d$, a quartet Γ_8 at $2c-16d$ and a doublet Γ_6 at $14c-20d$. The $J=5/2$ level similarly splits into a quartet Γ_8 at $-4c$ and a doublet Γ_7 at $+2c$. The constants c and d are constants of the crystal field potential and signify the 4th and 6th order contribution. It is expected that c will be negative in the case of f^1 electrons (Ce^{3+}) and positive in the case of f^{13} electrons (Yb^{3+}) for eight coordinated compounds. The lowest level in our case will therefore be the Γ_7 doublet.[2,3]

The effect of an external magnetic field H on these levels is easily calculated. Closed expressions can be given for the [100], [110], and [111] directions. Assuming that the separation of the various Γ levels is larger than $\Lambda\beta H$ where Λ is the Lande g factor (8/7 in the case of Yb^{3+}), these expressions can be expanded in power of $\Lambda H/c$. They yield linear Zeeman effect splittings of

$$\begin{aligned}&\Gamma_7: -18c-12d\pm\tfrac{3}{2}\Lambda H\beta,\\ &\Gamma_8: 2c-16d\pm\tfrac{1}{6}\Lambda H\beta[65\pm8(49-135\Phi)^{\frac{1}{2}}]^{\frac{1}{2}},\\ &\Gamma_6: 14c-20d\pm(7/6)\Lambda H\beta,\end{aligned}\qquad(1)$$

where $\Phi=l^2m^2+m^2n^2+l^2n^2$ are the direction cosines of the external field with respect to the cubic axes. The significant aspect is that the lowest level gives an iso-

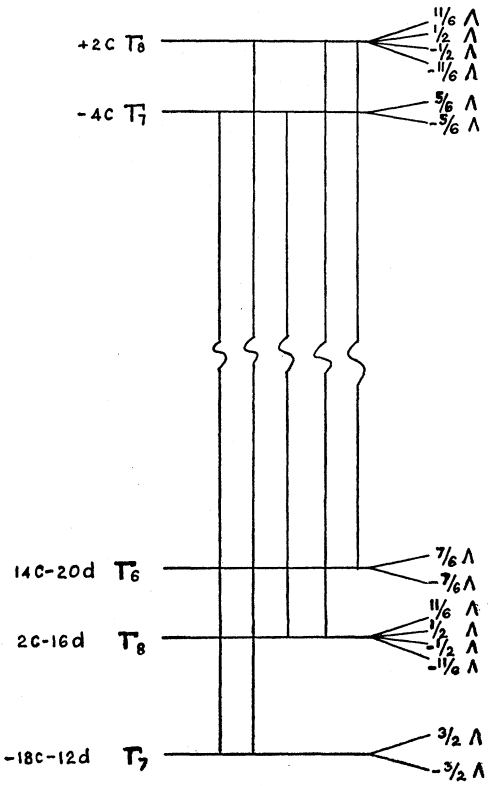

FIG. 1. Energy level scheme of $^2F_{7/2}$ and $^2F_{5/2}$ states of Yb^{3+} in a cubic field. The left-hand side indicates the initial splittings in units of the fourth and sixth order cubic potentials c and d. The diagram is drawn to scale assuming $d\ll c$. The right hand side shows the effect of a magnetic field. The g factors are indicated in units of $\Lambda=8/7$. The transition indicated between the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ states are those permitted by magnetic dipole selection rules.

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tropic g factor of 3Λ or 24/7. The next level will give rise to anisotropic g factors which along the [100] directions have values $(22/6)\Lambda$, 2Λ, $(10/6)\Lambda$, and Λ. Figure 1 shows the splittings of the various levels.

The lowest level Γ_7 can be expressed in a cubic spin Hamiltonian

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{I}\cdot\mathbf{S} \text{ with } S=1/2 \text{ and } g=3\Lambda. \quad (2)$$

The transitions are given by

$$H=H_0-Am[1+(A/2H_0)^2]$$
$$-(A^2/2H_0)[I(I+1)-m^2], \quad (3)$$

in which $I=1/2$ for Yb^{171} and 5/2 for Yb^{173}. The correction in the first bracket is the perturbation carried to third order which proved to be necessary since the g factor is relatively large.

A single crystal of CaF_2 with about 0.05% by weight of ytterbium fluoride was grown in a manner previously described.[1] A spectrum was observed at 20°K and at 3 cm wavelength. The spectrum showed an intense line at $g=3.426\pm0.001$ flanked by hyperfine structure components with an interval of $\Delta_1^{171}=566.1\pm1.5$ and $\Delta_2^{173}=763.2\pm1.5$ gauss where Δ_2 measures the interval between the $m=\pm5/2$ components. Correcting to third order [see Eq. (2)] we find $A^{171}=(886.5\pm1.5)\times10^{-4}$ cm^{-1} and $A^{173}=(243.2\pm0.4)\times10^{-4}$ cm^{-1}. The ratio of the magnetic moment $\mu^{173}/\mu^{171}=1.3749\pm0.005$. Determining $\langle1/r^3\rangle$ from the observed fine structure splitting in this crystal[4] we find $|\mu^{171}|=0.41_3\pm0.05$ and $|\mu^{173}|=0.57\pm0.05$. The ratio of $A^{171}/g=2.587\times10^{-2}$ is a few percent lower than that found by Cooke and Park (2.669×10^{-2}).[5] This crystal promises to be a suitable host for measurements on γ-γ correlation of radioactive ytterbium nuclei as well as a possible material for Mössbauer type experiments.[6]

In addition we found a number of weaker lines with total intensity less than 10% which were highly anisotropic and not all of which showed an extremum along one of the cubic axes. The nature of these lines will be investigated further; in part they arise from ytterbium surrounded by an axial field. The strongest of the anisotropic lines was found to have a g factor of 1.47 which could possibly be the transition within the Γ_8 quartet, I.e., the transition between

$$(7/12)^{\frac{1}{2}}\Psi_{\pm7/2}-(5/12)^{\frac{1}{2}}\Psi_{\pm1/2}\rightarrow(\tfrac{3}{4})^{\frac{1}{2}}\Psi_{\pm5/2}+(\tfrac{3}{4})^{\frac{1}{2}}\Psi_{\pm3/2}$$

which gives a g factor of $(32/21)\Lambda\sim1.52$.

The optical spectrum was investigated at room and liquid air temperature. In the visible and ultraviolet spectrum we observed strong bands and lines which are transitions to a different configuration. In the near infrared, lines were found at 9774, 9770, and 9763 A, flanked by a number of weaker lines. In addition there are diffuse and unresolved bands at 9080 and 12370 A. The expected transitions for magnetic dipole selection rules are indicated in Fig. 1. This would give rise to an optical crystal fine structure spectrum at $20c+12d$, $14c+12d$, $-6c+16d$, $16d$, $-12c+20d$. Since we do not know the relative magnitude of c and d nor the exact nature of the selection rules it is difficult to fit 3 lines to 5 or more predicted transitions. At any rate the total separation is $32c-8d$ and this equals to the $\Gamma_8-\Gamma_6$ separation of the ground state. Experimentally this separation is found to be about 12 cm^{-1}. It is seen, if this interpretation is correct, that the cubic field is relatively weak and that the initial splitting is not very much larger than the Zeeman energies usually used in electron spin resonance experiments. It is to be noticed that Dieke and Crosswhite[7] find absorption lines at 9708.8 and 9722.8 A or a splitting of about 15 cm^{-1} in the crystal field of triclinic ytterbium trichloride. This is of the same order of magnitude as that found by us. On the other hand the relative intensity of the weaker paramagnetic absorption lines indicate a larger splitting.

Further work at 4°K and using a high resolution spectrometer is being planned.

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