Paramagnetic Resonance of Trivalent Holmium Ions in Calcium Tungstate

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Paramagnetic resonance has been observed in calcium tungstate containing trivalent holmium ions in sites with tetragonal symmetry. The observed spectrum was fitted to the spin Hamiltonian $\mathcal{H}=g_{\parallel}\beta H\cos\theta S_z+\Delta_x S_x+\Delta_y S_y+AS_zI_z$ with $A=0.299$ cm^{-1} and $g_{\parallel}=13.691$. The distortion parameter $\Delta=(\Delta_x^2+\Delta_y^2)^{1/2}$ did not possess a unique value and consequently the absorption line shape was asymmetric, the value of Δ corresponding to the peak intensity being 0.03 cm^{-1}. These results for Ho^{3+} are contrasted with those published for Tb^{3+} in $CaWO_4$ and attention is drawn to the differences in line shape in the two cases. It is found that the lowest level in $CaWO_4/Ho^{3+}$ is of the type

$$\Psi=\phi|\pm7\rangle+\chi|\pm3\rangle+\psi|\mp1\rangle+\Omega|\mp5\rangle.$$

Finally, the results of paramagnetic-resonance measurements on all trivalent rare-earth ions in tetragonal sites in $CaWO_4$ are summarized in an Appendix.

1. INTRODUCTION

CALCIUM tungstate ($CaWO_4$) crystals, grown from a melt containing 0.1% of a trivalent rare earth and 1.5% of sodium, exhibit only tetragonal paramagnetic-resonance spectra,[1] the rhombic or "anomalous"[2] spectra being absent. There is good evidence that the tetragonal spectrum, first reported by Hempstead and Bowers[3] for $CaWO_4$/Gd:Na, is due to the rare-earth ion in a Ca^{2+} site, the charge compensator being at sufficiently long range for the S_4 symmetry of the nearest-neighbor crystal field to be undisturbed. A point-charge calculation for Yb^{3+} in a Ca^{2+} site,[4] using parameters obtained from spin-resonance measurements,[5] gives predictions of the $^2F_{5/2}\leftrightarrow{}^2F_{7/2}$ optical transitions which are in quite good agreement with experiment. The experiments described by Nassau and Loiacano[6] on coupled substitution add further weight to the argument in favor of rare-earth substitution into Ca^{2+} sites when an excess of sodium is present.

With the exception of Tb^{3+}, all spin-resonance studies of rare-earth ions in $CaWO_4$ which have been reported have related to Kramers ions. A search at 9 Gc/sec (X band) and 36 Gc/sec (Q band) has failed to reveal spin resonance from Pr^{3+} and Tm^{3+}, but Ho^{3+} has yielded a spectrum which shows interesting differences from that reported by Forrester and Hempstead[7] for Tb^{3+} ions.

The $(2J+1)$-fold degenerate ground manifolds of free, non-Kramers ions are converted in an electric field of S_4 symmetry into a system of singlets and doublets, the latter corresponding to pairs of singlet representations which are degenerate with respect to time reversal. In practice the two lowest crystal-field levels are generally singlets which either arise (a) normally in pure S_4 symmetry or (b) result from Jahn-Teller splitting of a time-reversed doublet. It will be shown how the Tb^{3+} resonance described by Forrester and Hempstead arises from transitions between singlets of type (a) whereas the results to be presented for Ho^{3+} relate to transitions between singlets of type (b).

2. Tb^{3+} AND Ho^{3+} IN AN ELECTRIC FIELD WITH S_4 SYMMETRY

The eigenfunctions of a free rare-earth ion can be used as a basis for the representation $D^{(J)}$ of the full rotation group in three dimensions (R_3). The eigenfunctions of a non-Kramers ion in a Ca^{2+} site form bases for the single-valued representations[8] $^1\Gamma_1$ to $^1\Gamma_4$ of the point group S_4, $^1\Gamma_3$, and $^1\Gamma_4$ corresponding to time-reversed states. The ground configurations of Tb^{3+} and Ho^{3+} are $(4f)^8$ and $(4f)^{10}$ and the lowest free-ion manifolds which have $J=6$ and $J=8$, respectively, split up in S_4 symmetry as follows:

$$Tb^{3+}\quad {}^7F_6\rightarrow 3{}^1\Gamma_1+4{}^1\Gamma_2+3({}^1\Gamma_3+{}^1\Gamma_4),$$
$$Ho^{3+}\quad {}^5I_8\rightarrow 5{}^1\Gamma_1+4{}^1\Gamma_2+4({}^1\Gamma_3+{}^1\Gamma_4).$$

S_4 is an Abelian group, so that the irreducible representations are all one-dimensional, and would all correspond to singlet states but for the time-reversal degeneracy of $^1\Gamma_3$ and $^1\Gamma_4$. In contrast to the case of Kramers ions, this residual degeneracy can be removed by electric fields of symmetry lower than S_4, so that when $(^1\Gamma_3,{}^1\Gamma_4)$ doublets lie lowest a Jahn-Teller distortion will split them into singlets. As Öpik and Pryce[9]

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[1] See Appendix for summary of parameters of tetragonal ESR spectra of trivalent rare-earth ions in $CaWO_4$.

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have pointed out, there will generally be a number of differently oriented but equivalent versions of the distortion, and a particular center may interchange rapidly between them if the sample temperature is high enough. However, if the thermal energy is lower than the energy required for interchange, the whole rare-earth-ion population will be frozen into an equal distribution among the various possible distortions.[10]

In cases where the zero-field splitting is smaller than a microwave quantum, paramagnetic resonance may be observed and regardless of whether the levels involved are singlet states ($^1\Gamma_1$ or $^1\Gamma_2$) or Jahn-Teller split doublets ($^1\Gamma_3$,$^1\Gamma_4$), the results can be explained by the treatment of Baker and Bleaney[11] who used the following spin Hamiltonian:

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\Delta_x S_x+\Delta_y S_y+AS_zI_z+B(S_xI_x+S_yI_y),$$

where the quadrupole and direct magnetic field-nuclear interactions have been neglected. The first term represents the Zeeman Effect of a dc magnetic field (H) acting on an effective spin $S(=\frac{1}{2})$. The second and third terms describe the zero-field splitting and the remaining terms refer to the hyperfine interaction. In the cases of Tb^{3+} and Ho^{3+}, $g_\perp$ and B are zero to within experimental error so that

$$\mathcal{H}=g_{\|}\beta H\cos\theta S_z+\Delta_x S_x+\Delta_y S_y+AS_zI_z; \quad (1)$$

and when $S=\frac{1}{2}$, resonance occurs at frequency ν given by

$$H=\{[(h\nu)^2-\Delta^2]^{1/2}-Am\}/g_{\|}\beta\cos\theta, \quad (2)$$

where $\Delta^2=\Delta_x{}^2+\Delta_y{}^2$ and m is the resolved component of the nuclear-spin quantum number I.

When the transitions are of type (a), Δ represents the static zero-field splitting (C) between singlets of the type $^1\Gamma_1$ or $^1\Gamma_2$, and a symmetrical resonance line is observed. However, if a ($^1\Gamma_3$,$^1\Gamma_4$) doublet is lowest there is a dynamic Jahn-Teller splitting δ, where δ has a Gaussian error distribution about zero, and the type (b) resonance is observed at

$$H=\{[(h\nu)^2-\delta^2]^{1/2}-Am\}/g_{\|}\beta\cos\theta.$$

Provided that $(h\nu)^2$ is not too much greater than δ^2 the line will be asymmetric about the $\delta=0$ point, being pulled out on the low-field side because the sign of δ is immaterial. The $\delta=0$ point is the zero intensity point (Ref. 11) and maximum intensity occurs when $\delta=\delta_0$, the parameter which controls the range of the distribution of δ. In the absence of any other significant line-broadening mechanism, a measurement of the splitting between the $\delta=0$ and $\delta=\delta_0$ points gives a value for δ_0.

In the case of Tb^{3+}, the line shapes observed by Forrester and Hempstead were symmetrical down to about 8 Gc/sec,[12] indicating the existence of a static splitting C between $^1\Gamma_1$ or $^1\Gamma_2$ singlets. In fact, because the observed g value (17.777) was very close to the maximum possible value of 18 corresponding to a $J_z=\pm 6$ doublet, Forrester and Hempstead were able to identify the two lowest levels as $^1\Gamma_2$. For Ho^{3+}, it has been found that the lines are asymmetric at 9 Gc/sec suggesting that $C=0$ and that the lowest level in S_4 is a ($^1\Gamma_3$,$^1\Gamma_4$) doublet, split by Jahn-Teller distortion. (See Table I.)

TABLE I. Eigenvectors of Tb^{3+} and Ho^{3+} in S_4 symmetry.

	$Tb^{3+}(J=6)$	$Ho^{3+}(J=8)$
$^1\Gamma_1$	$a\|4\rangle+b\|0\rangle+c\|-4\rangle$	$r\|8\rangle+s\|4\rangle+t\|0\rangle+u\|-4\rangle+v\|-8\rangle$
$^1\Gamma_2$	$d\|6\rangle+e\|2\rangle+f\|-2\rangle+g\|-6\rangle$	$w\|6\rangle+x\|2\rangle+y\|-2\rangle+z\|-6\rangle$
$^1\Gamma_3$	$\alpha\|5\rangle+\beta\|1\rangle+\gamma\|-3\rangle$	$\phi\|7\rangle+\chi\|3\rangle+\psi\|-1\rangle+\Omega\|-5\rangle$
$^1\Gamma_4$	$\alpha\|-5\rangle+\beta\|-1\rangle+\gamma\|3\rangle$	$\phi\|-7\rangle+\chi\|-3\rangle+\psi\|+1\rangle+\Omega\|+5\rangle$

In the following section, the new observations of Ho^{3+} will be described and it will be seen that the general form of the lowest levels can again be found.

3. THE PARAMAGNETIC RESONANCE SPECTRUM OF Ho^{3+} IONS IN $CaWO_4$

The samples were cut from material which was pulled from a melt containing 0.1% of holmium and 1.5% of sodium. Resonance was observed at 4.2°K and below with spectrometers operating at X band and Q band. The simplest spectrum was that observed at Q band with the dc magnetic field H and the rf magnetic field H_1 both parallel to the c axis of the sample. Eight symmetrical, equally spaced hyperfine lines were observed (as was expected) for holmium which has a 100% abundant isotope Ho^{165} with nuclear spin $I=\frac{7}{2}$. The lines, which were about 10 G wide, moved to higher fields and broadened considerably when the angle θ between H and the c axis was increased from zero. At $\theta=\pi/2$ no lines were observed irrespective of whether H and H_1 were mutually parallel or orthogonal. Because of line broadening with increasing θ, no measurements beyond $\theta=70°$ were possible, and at angles less than 70° the experimental accuracy of the line positions was poor. As a result, one can only say that plots of the center of gravity of the spectrum and of hyperfine splitting versus $\sec\theta$ were not inconsistent with the supposition that Ho^{3+} is a normal non-Kramers ion in having $g_\perp$ and B of the order of zero. The total loss of the spectrum at $\theta=\pi/2$ is again consistent with $g_\perp=0$. When the observed spectrum was fitted to the spin Hamiltonian

[10] A good example of the study of the variation in the behavior of a Jahn-Teller distortion with temperature is the work on Ni^- in germanium [G. W. Ludwig and H. H. Woodbury, Phys. Rev. 113, 1014 (1959)].

[11] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156 (1958).

[12] P. A. Forrester (private communication).

[Eq. (1)], the values $g_{\|}=13.691\pm0.006$ and $A=0.299\pm0.001$ cm^{-1} were obtained. Assuming negligible admixture into the ground manifold from the $^5I_7$ level, the above values of A and $g_{\|}$ can be used to estimate a value for the nuclear moment of Ho^{165}. Elliott and Stevens[13] have given the expressions

$$\mu_N=\{A\cdot I\langle J\|\Lambda\|J\rangle\}/2\beta\beta_N\langle J\|N\|J\rangle\langle r^{-3}\rangle_{\rm av}$$

and

$$\langle r^{-3}\rangle_{\rm av}=12(70-55)^{3/4}\ \text{Å}^{-3}=77\ \text{Å}^{-3}$$

and have tabulated the reduced matrix elements. Thus a value of $\mu_N=3.42$ nuclear magnetons is obtained in reasonable agreement with the value 3.29 published by Baker and Bleaney.[14]

The symmetrical line shape observed at Q band indicated the existence of either a static splitting C or a dynamic splitting δ which was small compared with $h\nu$. A plot of ν the microwave frequency versus H, constructed from Eq. (2) with $\Delta=0.04$ cm^{-1} (Fig. 1), shows that at X band the spectrum should be less simple, some hyperfine lines appearing twice and some not at all. The X-band spectrum obtained with H, H_1, and the c axis all parallel shown in Fig. 2 is seen to be consistent with this prediction. Furthermore, the lower experimental frequency has led to an asymmetry of the lines, indicating the existence of a dynamic Jahn-Teller splitting δ. The value of $g_{\|}$ obtained at X band by measuring the maximum slope point on the high-field side of the absorption-line derivatives was within experimental error of the Q-band value.

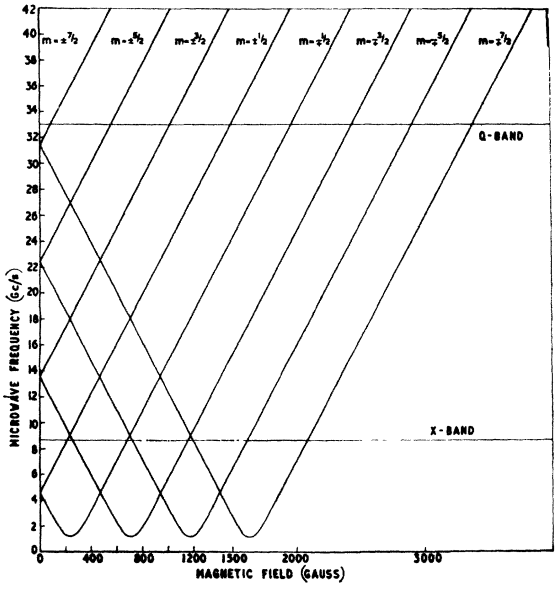

FIG. 1. The variation of the Ho^{3+} hyperfine line resonant frequencies when the dc magnetic field is parallel to the c axis.

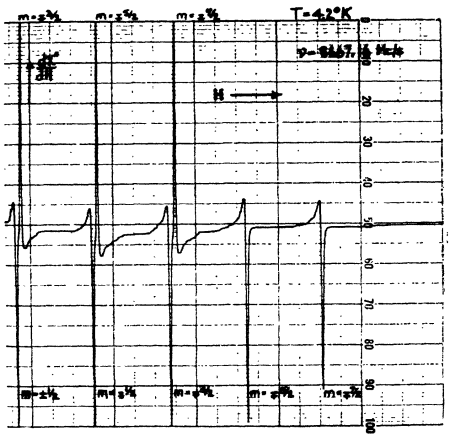

FIG. 2. X-band absorption-derivative spectrum of Ho^{3+} ions in $CaWO_4$ with H and H_1 parallel to the c axis. Note the asymmetry of the lines and their unusual disposition.

At X band, with the rf and dc magnetic fields parallel to the c axis, the width between $\delta=\delta_0$ and $\delta=0$ points was 8.4 G indicating a value of 0.05 cm^{-1} for δ_0. However, with H parallel to c and 80° away from H_1 the lines were less intense, as expected, but also narrower leading to a value $\delta_0=0.03$ cm^{-1}. A possible explanation of this difference is that when the line is almost forbidden, the spin-spin and spin-lattice broadening is reduced so that the latter value of δ_0 would be nearer to the correct value.

Finally, the large value of A leads one to expect simultaneous electron and nuclear flips when H_1 and H are mutually orthogonal. In fact, seven such transitions were observed in the expected locations half-way between the eight lines seen with H parallel to H_1.

CONCLUSION

The spectra of both Tb^{3+} and Ho^{3+} can be fitted to a spin Hamiltonian containing a distortion term Δ, but in the case of Tb^{3+} the Δ represents a static zero-field splitting (C) in pure S_4 symmetry. The Δ in the case of Ho^{3+} represents a Jahn-Teller splitting δ of levels which are degenerate in strict S_4 symmetry. Thus, the lowest levels of Ho^{3+} in $CaWO_4$ are of the type ($^1\Gamma_3$,$^1\Gamma_4$) or

$$\phi|\pm7\rangle+\chi|\pm3\rangle+\psi|\mp1\rangle+\Omega|\mp5\rangle.$$

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APPENDIX

Table II[15–18] gives the results of paramagnetic-resonance measurements on all trivalent rare-earth ions in tetragonal sites in $CaWO_4$.

TABLE II. g values and eigenvectors for trivalent rare-earth ions in tetragonal sites in calcium tungstate.

Ion	Ground manifold	Observed $g_{\parallel}$	Lowest level (derived from observed $g_{\parallel}$ assuming no mixing from higher manifolds)	Calculated $g_{\perp}$	Observed $g_{\perp}$	Irreducible rep^{r} in S_4	Reference
Ce^{3+}	$^2F_{5/2}$	2.915	$0.895\|\pm\frac{5}{2}\rangle+0.447\|\mp\frac{3}{2}\rangle$	1.534	1.423	$(^1\Gamma_5,^1\Gamma_6)$	5
Pr^{3+}	$^3H_4$	...	No ESR observed at 9 and 36 Gc/sec	...	...		This paper
Nd^{3+}	$^4I_{9/2}$	2.035	$0.6828\|\pm\frac{9}{2}\rangle+0.5407\|\pm\frac{1}{2}\rangle+0.4916\|\mp\frac{7}{2}\rangle$	[a]	2.533	$(^1\Gamma_7,^1\Gamma_8)$	15, 16
Pm^{3+}	$^5I_4$	...	...	...	...	...	...
Sm^{3+}	$^6H_{5/2}$	0.4396	$0.753\|\pm\frac{5}{2}\rangle+0.658\|\mp\frac{3}{2}\rangle$[b]	0.633	0.6416	$(^1\Gamma_5,^1\Gamma_6)$	17
Eu^{3+}	$^7F_0$	...	...	...	...	...	...
Gd^{3+}	$^8S_{7/2}$	1.9915	...	...	1.9916	...	3
Tb^{3+}	$^7F_6$	17.777	$a\|6\rangle+b\|2\rangle+c\|-2\rangle+d\|-6\rangle$	0	<0.15	$^1\Gamma_2$	7
Dy^{3+}	$^6H_{15/2}$	7.267	Data insufficient to obtain eigenvector	...	5.466	...	18
Ho^{3+}	$^5I_8$	13.691	$\alpha\|\pm7\rangle+\beta\|\pm3\rangle+\gamma\|\mp1\rangle+\delta\|\mp5\rangle$[c]	0	$\simeq0$	$(^1\Gamma_3,^1\Gamma_4)$	This paper
Er^{3+}	$^4I_{15/2}$	1.251	$\|\pm\frac{1}{2}\rangle$[d]	9.6	8.401	$(^1\Gamma_5,^1\Gamma_6)$	18
Tm^{3+}	$^3H_6$	...	No ESR at 9 and 36 Gc/sec	...	...	...	This paper
Yb^{3+}	$^2F_{7/2}$	1.055	$0.702\|\pm\frac{5}{2}\rangle+0.714\|\mp\frac{3}{2}\rangle$	3.969	3.914	$(^1\Gamma_5,^1\Gamma_6)$	5

[a] Both g values were needed to obtain the eigenvector so that there is no check on its correctness. However, $Ag_{\perp}/Bg_{\parallel}=0.97$ rules out mixing from $^4I_{11/2}$.
[b] The agreement between experimental and predicted values of $g_{\perp}$ is fortuitous. $Ag_{\perp}/Bg_{\parallel}=0.38$ indicates important mixing from $^6H_{7/2}$.
[c] In the absence of Jahn-Teller splitting.
[d] Predicted $g_{\parallel}$ for pure $|\pm\frac{1}{2}\rangle$ state is 1.200.

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Rare-Earth Ion Relaxation Time and G Tensor in Rare-Earth-Doped Yttrium Iron Garnet. I. Ytterbium

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Microwave-resonance measurements at 9.3 and 16.8 Gc/sec between 1.5 and 300°K in the principal crystallographic directions of a single-crystal of yttrium iron garnet (YIG) doped with 5.1% Yb are compared with the predictions of the longitudinal (so-called "slow relaxing ion") mechanism of relaxation, which is briefly reviewed. Except for the low-temperature anomaly in the [110] direction, excellent agreement is found. A quantitative analysis allows deduction of the tensor G describing the anisotropic exchange splitting of the ground-state Kramers doublet of the Yb ion. We obtain $G_1=31.9$ cm^{-1}; $G_2=22.4$ cm^{-1}; $G_3=8.5$ cm^{-1}, which is a similar result to that reported from spectroscopic measurements on ytterbium iron garnet. The small differences probably reflect the different lattice dimensions in the two cases. We also deduce τ, the relaxation time of the Yb ion in the YIG environment. The results are most extensive and accurate in the [111] direction, where the temperature dependence for $T<60$°K indicates the dominance of a direct process as described by $(1/\tau)_D=(1/\tau^0)_D\coth(\delta/2kT)$ with $(1/\tau^0)_D=2.1\times10^9$ sec^{-1} for $\delta_{111}=21.0$ cm^{-1}. Taking into account that the measured relaxation time in this direction is a weighted average of the two relaxation times associated with the two values of the doublet splitting, we find that the observed direct process is well described by spin-magnon relaxation, which also gives a more consistent evaluation of the G tensor than does spin-lattice relaxation. At higher temperatures, the temperature dependence of the observed relaxation time follows that expected for the Raman process, viz., $(1/\tau)_R=AJ_8T^9$, with $A=4.5\times10^{-12}$ sec^{-1} (°K)$^{-9}$ for a Debye temperature of 550°K. This is in excellent agreement with the Raman-process relaxation time reported for Yb in yttrium gallium garnet, though it is some 5 orders of magnitude shorter than the theoretical estimate. The Orbach process is found to be unimportant over the temperature range covered.

1. INTRODUCTION

THE presence of small amounts of rare-earth (RE) ions profoundly modifies the ferrimagnetic resonance properties of YIG (yttrium iron garnet). Thus the resonance linewidth ΔH is considerably broadened, and depends in a complicated way on temperature, microwave frequency, and crystallographic direction. Furthermore, the value of the applied field for resonance

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