Absorption of Circularly Polarized Light by the $^4A_2 \to {}^2E$ and $^4A_2 \to {}^2T_2$ Transitions of Ruby in Strong Magnetic Fields

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The longitudinal Zeeman effects exhibited by the R and B lines of ruby have been measured at 80 K using circularly polarized light and magnetic fields up to 200 k gauss. By employing as a standard the EPR-determined value for $g\|(^4A_2)$ of 1.984 and a method that is independent of the absolute magnitude of the magnetic field, analysis of the R lines gives $g\|(\bar{E}(^2E)) = 2.49 \pm 0.02$, $g\|(2\bar{A}(^2E)) = 1.41 \pm 0.02$ and $\Delta = 0.37 \pm 0.03$ cm^{-1}. Corresponding results derived from the B lines are: $g\|(2\bar{A}(^2T_2)) = 0.58 \pm 0.02$ and $g\|(E_a(^2T_2)) = 2.90 \pm 0.05$, consistent with values published previously.

1. INTRODUCTION

The observation of magnetic circular dichroism (MCD) is increasingly being used as a supplementary method to absorption spectroscopy in the study of transition metal complexes.[1] In the usual MCD experiments the magnetic field is constant, the polarization of the light beam is modulated between left-handed (LH) and right-handed (RH), and the difference in the absorption for the two polarizations is recorded. It is, of course, possible to measure the magnetic circular dichroism simply by performing a longitudinal Zeeman experiment with circularly polarized radiation in which Zeeman absorption spectra are recorded separately for the two polarizations LH and RH using a procedure analogous to that normally employed in crystal spectroscopy to measure linear dichroism. In theory, the difference between these two spectra is the MCD spectrum, while their sum gives the linear polarized axial Zeeman absorption spectrum. The method has the advantage that Zeeman components with $\Delta M = +1$ appear only in

LH spectra while those with $\Delta M = -1$ appear only in RH spectra. Estimates of the positions of such components can be made more easily than can the splittings of incompletely separated lines. In addition, measurement of line intensity is facilitated by the removal of light of opposite polarization from the background.

The Zeeman absorption spectrum due to the $^4A_2 \to {}^2E$ transition of Cr^{3+} in 2[Cr(en)₃Cl₃].KCl.6H₂O has recently been investigated using circularly polarized light,[2] and accurate g values for the excited states were derived. It seemed worthwhile to extend this study to other crystals containing Cr^{3+} in trigonal coordination, and also to other transitions found in these systems. The present paper describes some high magnetic field spectra of the spin-forbidden $^4A_2 \to {}^2E$ and $^4A_2 \to {}^2T_2$ transitions of Cr^{3+} in the host lattice Al₂O₃ (ruby). Since both these transitions have been examined both theoretically[3-6] and by other experimental techniques[7-11] the project appeared to be a good test of our method as well as existing theoretical models.

2. THEORY

The combined action of a trigonal crystal field component and the spin-orbit coupling split the ^2E state of Cr^{3+} in ruby into two Kramers doublets, $\bar{E}$ and $2\bar{A}$. The $\bar{E}$ sub-level lies at a lower energy than does the $2\bar{A}$ level.[3,8] Similarly the $^2T_2$ state is split into three components $2\bar{A}$, $\bar{E}_a$ and $\bar{E}_b$, while the $^4A_2$ ground state is split into two Kramers doublets separated by 0.38 cm^{-1}.[7] $g\|$ values (H parallel to the threefold axis) for all these levels except

$E_b(^2T_2)$ have been estimated from the results of Zeeman experiments using linearly polarized light.[7,9,10] The published experimental values vary over a broad range. Of these only $g\|(\bar{E}(^2E))$ has been determined very accurately by a paramagnetic resonance technique.[8] The $^4A_2 \rightarrow {}^2T_2$ system of transitions has been studied in a low field MCD experiment conducted at room temperature and at low resolution.[11]

The crystal field theory for this chromophore, first treated by Sugano and Tanabe,[3] has been continuously extended with the concurrent introduction of more and more adjustable parameters. Sugano and Peter,[4] for example, included parameters for covalency and for mixing between the $t_2{}^3$ and $t_2{}^2e$ configurations. The earlier work has recently been criticized and new g values have been computed using a numerical method based on the use of a set of functions of the complete d^3 configuration.[6] The relatively large errors in some of the experimental data have made comparisons of these theories quite difficult.

3. EXPERIMENTAL

Two crystals containing 0.15 mol % and 0.41 mol % of Cr^{3+}, respectively, were cut into plates with faces perpendicular to the c axis. They were oriented using X-ray diffraction methods. The spectroscopic technique was as described previously;[2] that is, the sample temperature was 77 K. The R lines ($^4A_2 \rightarrow {}^2E$) were recorded on 35 mm Kodak High Speed Infrared Film and on Kodak 103F plates. For the B lines ($^4A_2 \rightarrow {}^2T_2$) Ilford HP3 plates and Polaroid 4 × 5 Land Film, Type 57, were used. The magnetic field was calibrated using the ground state $g\|$ value of ruby determined by EPR.[12]

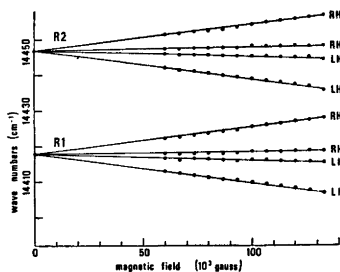## 4. RESULTS FROM THE R-LINES

Figs 1 and 2 show the experimentally observed splitting pattern of the R lines and the corresponding transition diagram, respectively. From the order of the components with decreasing energy, namely RH, RH, LH, LH for both R1 and R2, it follows that $g\|(2\bar{A}(^2E)) < g\|(^4A_2) < g\|(\bar{E}(^2E))$. Each pair of LH − RH exposures permits field-independent determinations of the ratios $g\|(\bar{E}(^2E))/g\|(^4A_2)$ and $g\|(2\bar{A}(^2E))/g\|(^4A_2)$ and of the zero-field splitting. By using $g\|(^4A_2) = 1.984$ [12] and the averages from 13 pairs of exposures, the $g\|$ values shown in Table 1 were derived. The $g\|(\bar{E}(^2E))$ result presented here is within two estimated standard deviations of the low field value determined by EPR (2.445 [8]). The agreement of the zero field splitting Δ with corresponding values determined from EPR and a low field Zeeman experiment is also good.[7] However, the present g factors do not agree particularly well with values previously obtained from high field Zeeman experiments with linearly polarized light.[9]

The present results do not show any evidence of non-linearity of the splitting with the magnetic field for fields between zero and 170 k gauss.

A LH-RH pair of microdensitometer tracings is shown in Fig. 3. The relative intensities do not resemble those calculated,[3] even with the Boltzmann distribution accounted for.

Figs 2 and 3 clearly demonstrate that in this case more information can be gained using circularly polarized rather than linearly polarized light. The two heavily overlapping

Fig. 1. Splitting patterns observed for the R lines. R1 = $^4A_2 \rightarrow \bar{E}$ (^2E); R2 = $^4A_2 \rightarrow \bar{2}A(^2E)$.

Table 1. Δ values and numerical values for $g\|$.

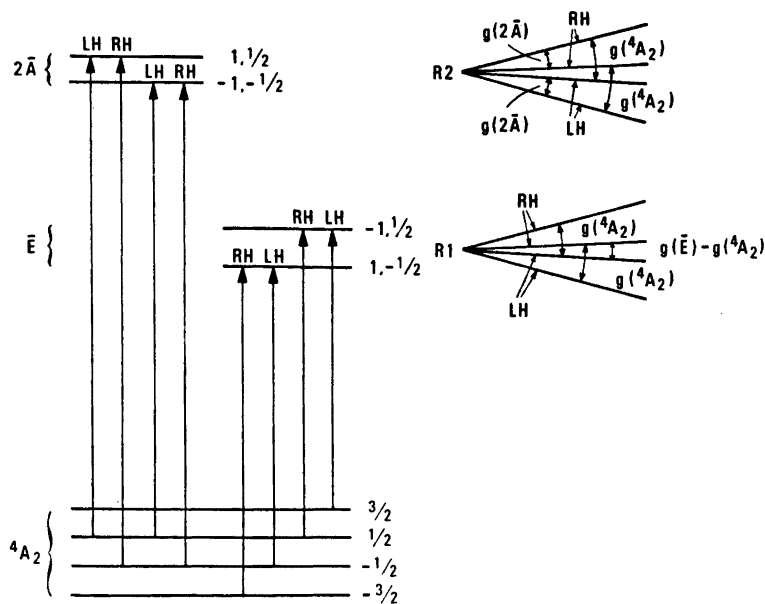|	Ours	Ref. 9	Ref. 6	Ref. 4
$g\|(\bar{E}(^2E))$	2.49 ± 0.02	2.56 ± 0.16	2.67	2.59
$g\|(2\bar{A}(^2E))$	1.41 ± 0.01	1.63 ± 0.13	1.21	1.23
$g\|(2\bar{A}(^2T_2))$	0.58 ± 0.02	0.69 ± 0.09	0.65	0.96
$g\|(\bar{E}_a(^2T_2))$	2.90 ± 0.05	2.97 ± 0.15	3.39	2.97
Δ in cm^{-1}	0.37 ± 0.03		0.31	0.16

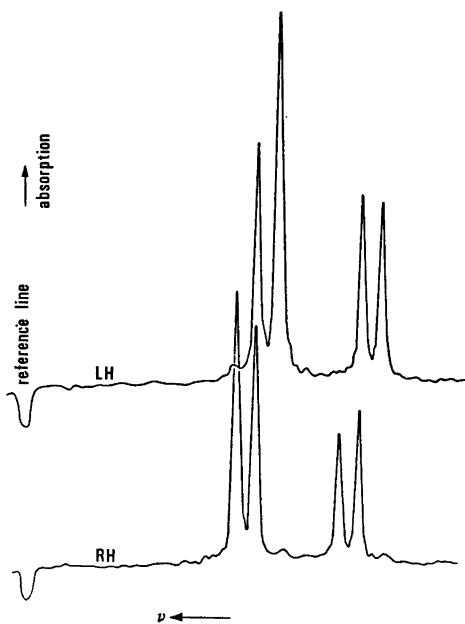**Fig. 2.** Transition diagram for the R lines.

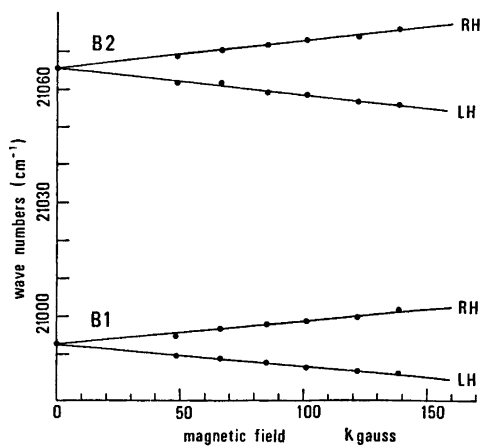**Fig. 3.** Microdensitometer tracing of the R lines at H = 97 k gauss.

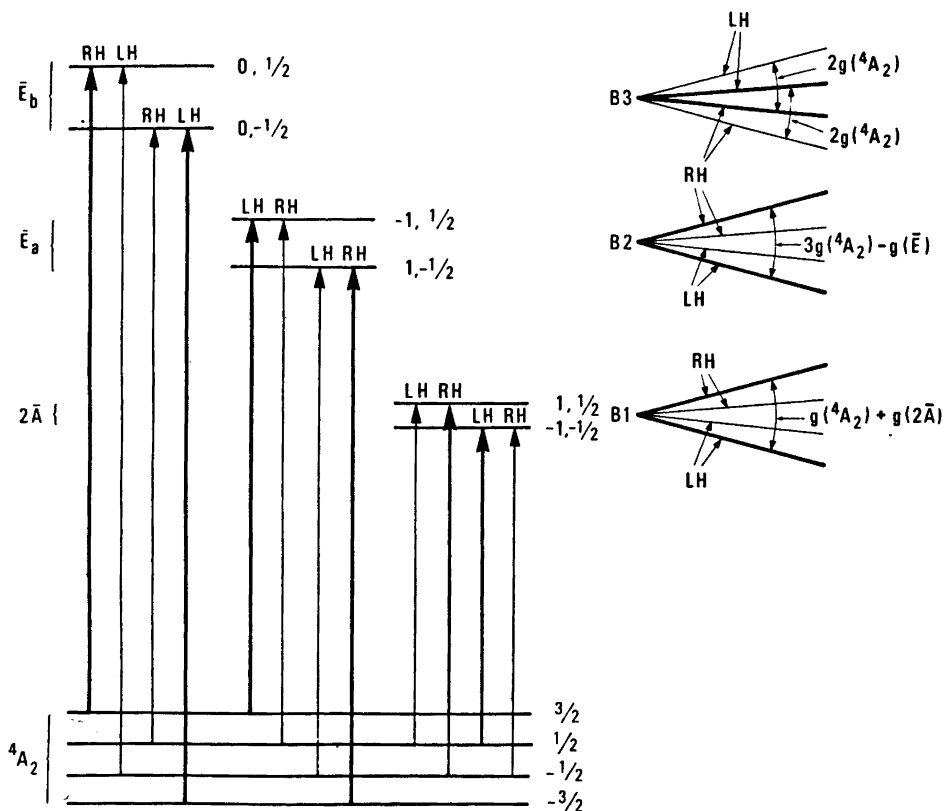**Fig. 4.** Splitting patterns observed for the B lines.

Fig. 5. Transition diagram for the B lines.

inner components in both R1 and R2 Zeeman patterns are of opposite polarization and can thus be resolved. This has led to $g\|$ values which are more accurate than those resulting from corresponding Zeeman experiments using linearly polarized light.[9] The separation also enables reliable estimates of the relative intensities of the components to be made.

5. RESULTS FROM THE B-LINES

The splitting pattern of the B1 and B2 lines is shown in Fig. 4 and the corresponding transition diagram for all three B lines is given in Fig. 5. As expected for both B1 and B2 the high energy component has RH polarization. The splitting pattern of B3 could not be fully resolved but it was possible to establish beyond doubt that a LH component is on the high energy side, in accordance with Fig. 5 and an

earlier low field MCD experiment. A straight line plotted through the experimental points obtained for magnetic fields up to 140 k gauss leads to the g values shown in Table 1. These are in agreement with those obtained previously.[9] To determine $g\|(\bar{E}_b(^2T_2))$ either a very strong magnetic field or a careful analysis of the line shape is necessary. Neither could be achieved under the conditions of the present study.

From Figs 4 and 5 it is clear that for B1 and B2 no overlapping lines can be resolved using circularly polarized light. Only the sign of ΔM has not already been determined earlier.[9]

6. DISCUSSION

Our experimental results are seen to be in better overall agreement with the crystal field theoretical predictions of Sugano and Peter [4] than with those made by Macfarlane.[6] Since

the number of adjustable parameters was six in both these calculations, the present experimental ruby values do not appear to substantiate Macfarlane's claim that his perturbation treatment gives accurate results. However, as Macfarlane points out, comparison with other systems is necessary before a definite assessment can be made; there does, in fact, seem to be better agreement between his values and experimental results obtained from other Cr^{3+}-doped lattices.

7. CONCLUSION

Measurements of the longitudinal Zeeman effect of the R and B lines of ruby using circularly polarized light have given information which previously had been obtained only from two independent experiments. The polarizations of all the observed transitions are in accordance with the theoretical predictions. There is no reason to believe that the $g\|$ values are more accurate than those previously determined from "conventional" Zeeman experiments.

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