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

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The longitudinal Zeeman-splitting of the $^2T_2$ (E_b) state of ruby has been measured at 4.2 K and the relative dipole strengths of the components involved were found at 80 K. The results were obtained by combining a pulsed magnet and an optical multichannel analyzer. The g-factor was found to be 4.15 ± 0.09, while the intensity ratio at 20.4 Wb/m^2 (204 kgauss) was 0.7 ± 0.1 for right-, and 0.15 ± 0.09 for left-circularly polarized light. The dipole strength of the most intense component of the B3 line did not vary with the magnetic field.

The electronic transitions of Cr^{3+} in ruby have been subject to investigation for many years, and are now qualitatively very well understood.[1–5] A considerable contribution to this understanding has been obtained by means of data from the spin-forbidden transitions within the t_2^3-configuration. These are all slightly split for all but Kramers degeneracy, and a considerable amount of effort has been devoted to Zeeman-measurements on these lines. This has resulted in determination of the g-factors for the ^2E, the $^2T_2(E_A)$ and $^2T_2(A)$ components.[2,3,5–8] However, the three components of the $^2T_1$ and the E_B component of the $^2T_2$ have not yet been determined. This is mainly because the absorption-lines involved are so broad, that either extremely strong fields or a quite different technique than previously used would be necessary. The purpose of this paper is to report on the determination of the g-factor for the $^2T_2(E_B)$ state and on the relative electronic intensity of its components by a technique using circularly polarized light and a pulsed magnet.

THEORY

The splitting pattern for the transitions to the $^2T_2$ state, called the B-lines is shown in Fig. 1, and those to ^2E, the R-lines, in Fig. 2. The intensity of these lines is due to spin-orbit coupled quartet-character contributions of the wave functions, mainly from the nearby quartets.[1]

Of the B1 and B2 lines of Fig. 1, only the heavily drawn lines have been observed. These lines are so sharp, that they permit a determination of the g-factors. The calculated intensity ratio of the B3 absorption line components is 1:3,[1] the strong ones are shown with heavy lines in Fig. 1. This line is considerably broader, and no separation has been observed for fields up to 230 kgauss. The broadening is due to relaxation to the other components of the same state, with the same spin.[9] The separation in energy is very close to that of a phonon observed in emission as well as in excitation spectra of the R-lines.[10] This has been used to explain the fact that the B3 line is double.[11,12] Further structure of the B3 line could be caused by a localized phonon added to this phonon. This effect has been observed in emission, where a structure with a characteristic vibrational energy of approximately 35 cm^{-1} can be seen in the phonon-line.[13] Assuming now that the B3 line does not hide a vibrational line from any other component, it will be assumed, that its first order moment is practically independent of the phonons. This seems reasonable because the Zeeman-splitting changes the energy differences by about 50 cm^{-1}, while

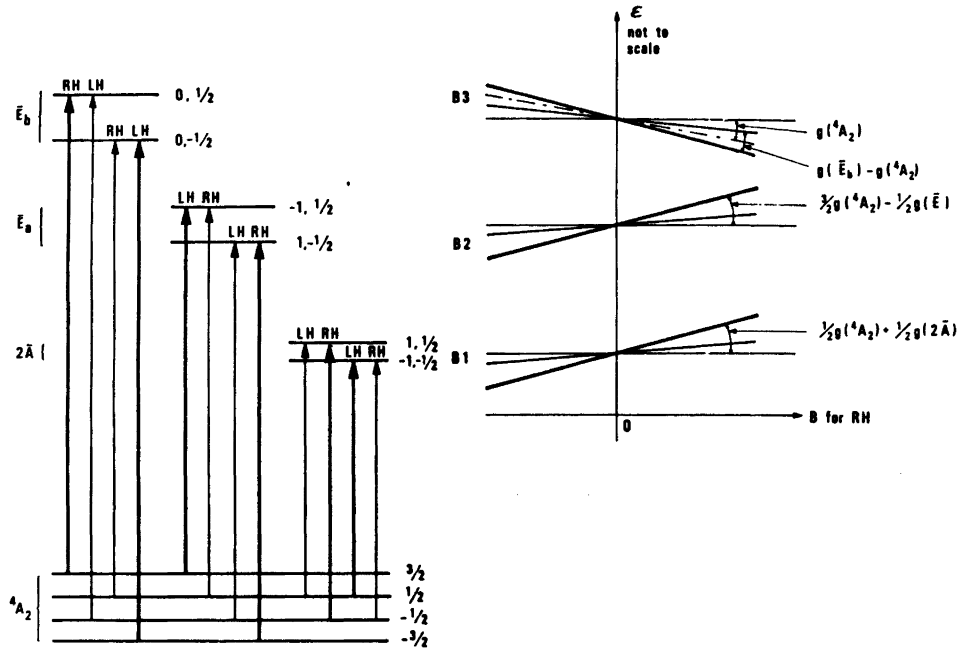

Fig. 1. Transition diagram and splitting pattern of the $^2T_2$ components.

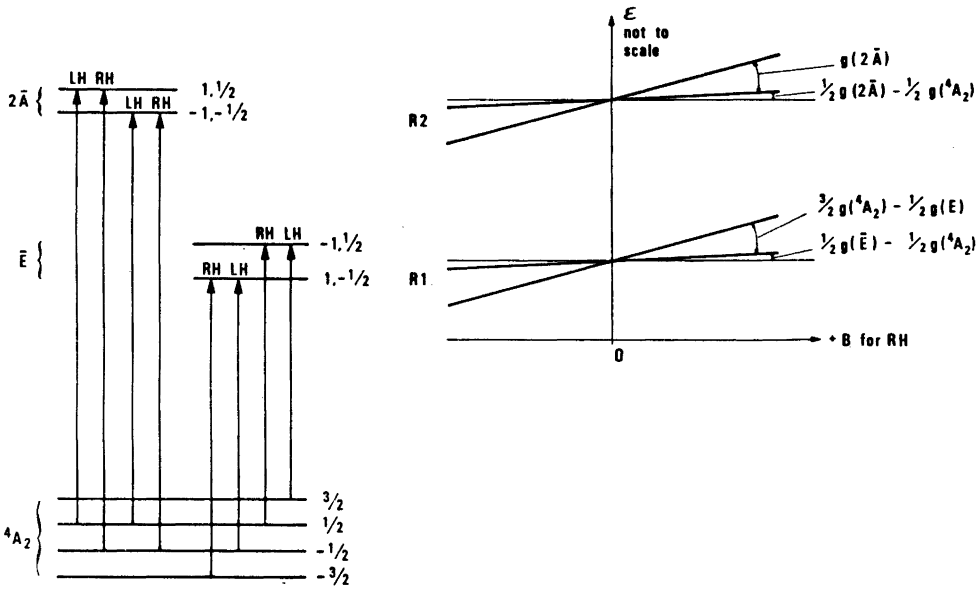

Fig. 2. Transition diagram and splitting pattern of the ^2E components.

resonance effects are expected to be within a few cm^{-1}.

The two components of each of the LH and RH circularly polarized spectra will be split by the amount $g-g_e$, and placed symmetrically with half this value above, and half below the value g. Here g is the ground state splitting, and g_e that of the excited state. The deviation of their common moment from g will therefore give information about their relative intensity and g_e. The intensity ratio is determined only by the electronic transition moment contribution and the ground state population.

EXPERIMENTAL

Two samples of ruby were used, one containing 0.15 mol % Cr^{3+}, and one 0.41 mol %. Only the last one, however, was used for the *B*-lines. The magnetic field was obtained by discharging a loaded capacitor through a small coil in which the sample was placed with its axis parallel to the field.[7] Light from a flash tube timed to fire at the maximum field was focused on the sample. Having passed parallel to the C_3-axis it was again focused through a circular polarizer on the spectrograph slit. The dispersed light was focused on the Videcon tube of an SSR Optical Multichannel Analyzer, where the spectra were stored on one of the two 500-channel digital memories. The other memory was used for dark current subtraction. The resolution at 5000 Å was two channels corresponding to 0.2 Å. Typically, however, a slitwidth of 1 Å was used, due to the limited sensitivety of the Videcon tube. Each spectrum was summed from 10 to 40 shots, and after accumulation, the spectra were transferred to a RC4000 computer. A background spectrum was also tranferred, to divide, channel by channel, into all spectra, before plotting and further data-handeling.

The set-up is shown in Fig. 3. A clock pulse goes to a unit built into the optical multichannel analyzer, OMA and is here stored until the next TV-frame retrace. Then the OMA is activated for one frame time, and a signal is sent to the switch to fire the magnet. When the magnet is fired, a signal goes to the flash-delay. This will fire the flash at the maximum of the field, and a spectrum will be collected. The firing has ended before the frame retrace is over and collection begins. The spectra are inspected on the oscilloscope which is also used to set the flash-delay.

Qualitatively the results are very clear, as seen of Fig. 4. which shows spectra recorded at 77 K for 35 different fields. The intensity variation of the B1 and B2 lines show clearly how the ground-state population changes with the Zeeman-splitting, which in a new way confirms the well-known transition diagram. The displacement of the B3 line goes the opposite way from that of the B1 and B2 lines, and excludes the possibility that the B3 line should be a vibration on one of these. The left circularly-polarized component gains slightly in intensity and remains narrow for higher fields, while the right-hand component

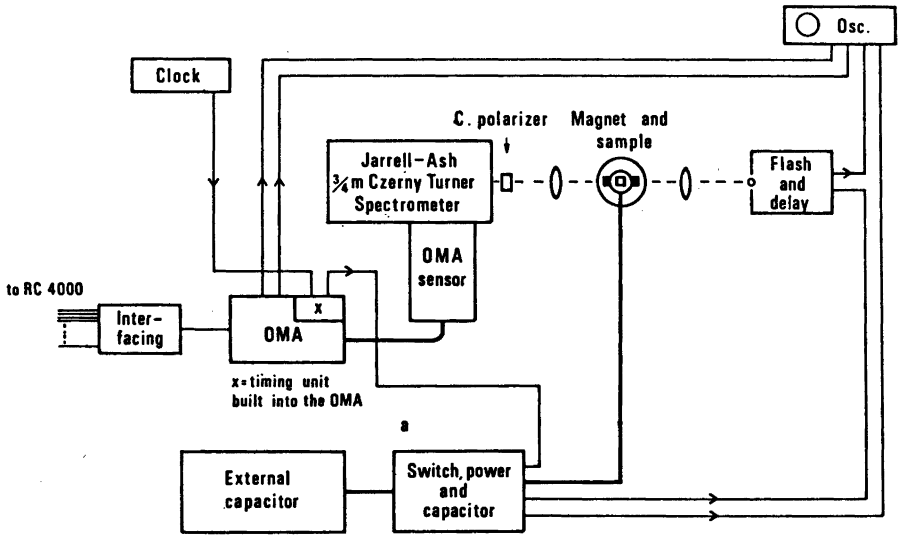

Fig. 3. The experimental set-up for recording pulsed-magnet Zeeman-spectra on an optical multichannel analyzer.

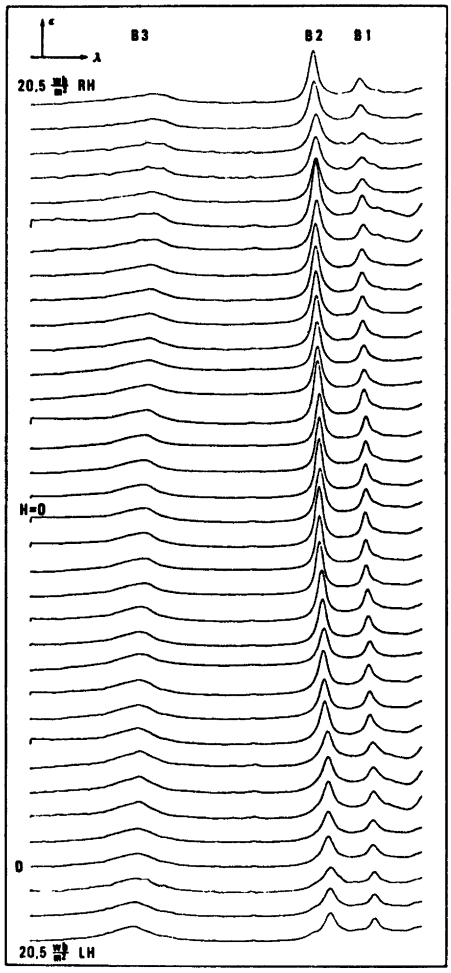

Fig. 4. Extinction coefficient as function of channel number (wavelength) of all three B-lines for 35 values of the magnetic field. One spectrum D was lost during data handling and has been replaced by its neighbour.

broadens and loses intensity. These facts confirm that the LH transition from the microstate with $S=-\frac{3}{2}$ has higher intensity than that from the state with $S=-\frac{1}{2}$, as the line will sharpen when the strongest component gains relatively in intensity, due to the ground state repopulation. Conversely the RH transition will have transferred intensity from the stronger to the weaker component, and a splitting will therefore result in a broadening.

Quantitatively the E_b-g-factor was determined from an experiment performed at 4.2 K, where practically all intensity was concentrated in the strongest LH component of the B3 line, and the RH component of the B2 line. The displacement of this component gave $g(^2T_2,E_b)=4.15\pm0.15$.

Fig. 5 shows a plot of the B3 line position as function of the applied voltage, together with the line whose slope is equal to the ground state splitting g. The spread of the points is considerable, but not enough to blur the apparent inconsistency of these results. The extreme RH end of the plot shows that the points are reasonably close to the line. As its point of gravity is determined by two components with equal distances from this line, the intensities of these components must be practically equal, and the change in dipole strength intensity contribution must therefore just cancel that of the population change. The population contributions were determined from the intensity ratios of the B1 and B2 lines of the same spectra and the zero-field spectrum. This ratio was closer to 1, than the ratio calculated considering a Boltzmann distribution.

The RH-side gave an electronic contribution to the weakest component of 0.7 times that of the strongest one practically independent of the $g(\bar{E}_b)$-factor. Using the liquid He temperature spectrum and the same population ratio, the electronic contribution from the LH spectrum was found to be 0.15, in clear disagreement with both the value found from the RH branch and the calculated electric dipole value of $\frac{1}{3}$.[1]

To check, whether a phonon-contribution could influence the displacement of the point of gravity of the B3 line, a new series of spectra were calculated from a set of original ones. The 35 spectra were added channel by channel after displacing the channel number by a parameter, p, multiplied by the magnetic field. Spectra were plotted for 35 values of p, including those matching the displacements of the B1 and B2 lines, but no special features could be seen at the B3-position for those p-values. This was taken as a strong evidence, that no phonons on the B1 and B2 lines contributed significantly to the B3 line. Further, if the displacement was partly due to the movement of such a contribution, the change of the $^2T_2,\bar{E}_b$-part must have been larger, as all other possible contributions move to the opposite side of that observed. Such a larger

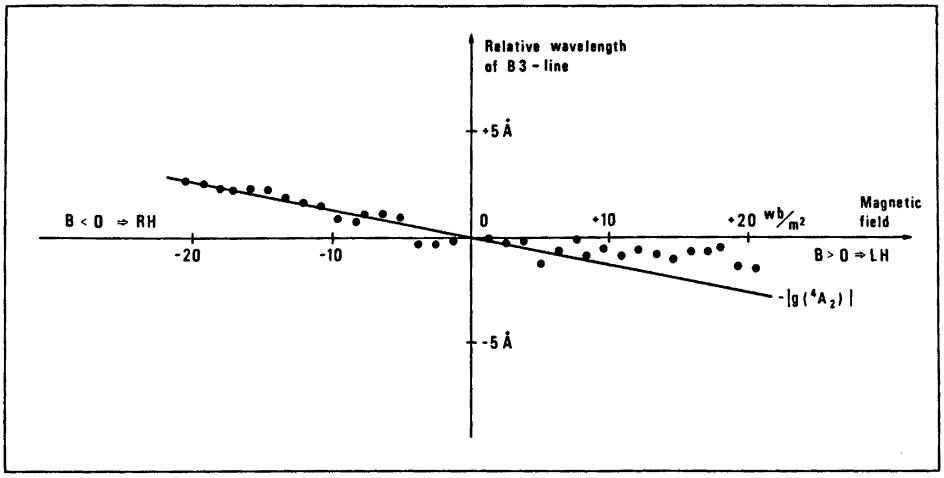

Fig. 5. Relative position of B3 line as a function of the magnetic field (points) compared to the ground state splitting (line).

change would, however, make the discrepancy worse. To check whether it was reasonable to use the B1 and B2 intensities for calculating the population ratio in the ground state, similar studies were made on the R-line spectra. These had to be recorded anyhow to calibrate the magnetic field.

The intensity ratios thus determined were in agreement with those obtained from the B lines for the fields used. For smaller fields, however, there seemed to be a threshold, below which the relaxation time was considerably longer than the firing time. No attempts were made, however, to determine the relaxation times as function of the splitting energy, as this would fall outside the scope of this work, and a modification of the magnet would be desirable to change the time dependence of the field from a cosine to a step-function.[14]

An interesting observation, not yet discussed, was that the two components of both of the R-lines were approaching different intensities when the magnetic field approached zero from either side. For the R1 line, the transitions from the microstates with $S = \pm\frac{1}{2}$ were 10 % higher than those from the states with $S = \pm\frac{1}{2}$, and of the R2 line, the components of the transition to the $1,\frac{1}{2}$-microstate were 10 % higher than those to the $1,-\frac{1}{2}$-microstate. For stronger fields, the Boltzmann distribution takes over, and the differences are

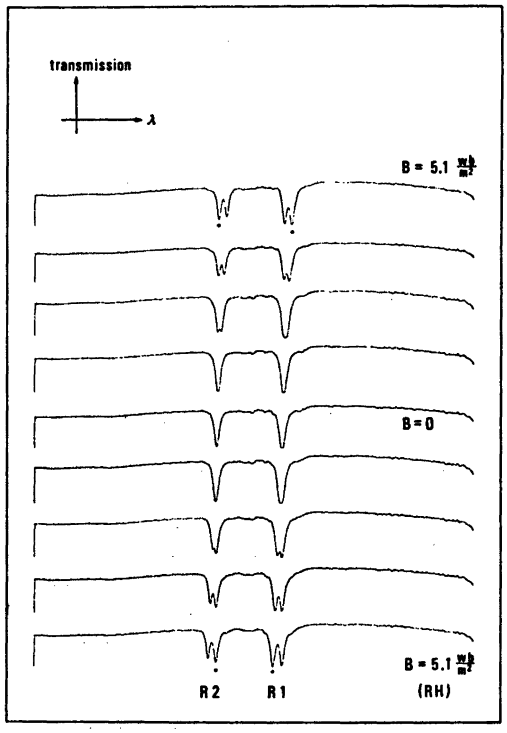

Fig. 6. Transmission of circularly polarized light by the R-lines for medium and small magnetic fields illustrating the intensity ratios between the components for H→0. The lines labeled · are those gaining intensity by ground state repopulation.

Table 1. Values for $g\|\|$ of Ruby doublet states.

	Ours	Ref. 8	Ref. 6	Ref. 4
$g\|\|[\bar{E}(^2E)]$	2.470 ± 0.003	2.56 ± 0.16	2.67	2.59
$g\|\|[2\bar{A}(^2E)]$	1.444 ± 0.003	1.63 ± 0.13	1.21	1.23
$g\|\|[2\bar{A}(^2T_2)]$	0.510 ± 0.005	0.69 ± 0.09	0.65	.96
$g\|\|[\bar{E}_a(^2T_2)]$	2.961 ± 0.005	2.97 ± 0.15	3.39	2.97
$g\|\|[\bar{E}_b{}^2T_2]$	4.15 ± 0.15			

blurred. To illustrate this, some low-field R-line spectra are shown in Fig. 6.

At present it seems hard to find any other explanation of the observed discrepancy, than to say that the dipole contribution to the B3 line components varies strongly with the magnetic field. In that case, however, the B1, B2 and R-line intensities cannot be used with confidence to scale the ground-state population, and this could just as well be considered to be the equilibrium value. But this modification will only lower the RH-result and raise the LH-result by 0.1, which is just the experimental standard deviation. From the intensity variation of the B3 line with the magnetic field, it was found that the dipole contribution to the strongest component was independent of the field within the experimental deviations. The g-values obtained from the experiments are shown in Table 1.

Experimentally the use of an optical multichannel analyzer has proven to be a great success in several aspects compared to the use of film. First the spectra can be observed immediately on an oscilloscope, and a lot of work with test-exposures is saved. Second the camera can be left in the same position through a long series of experiments, and the wavelength is thereby a well defined function of the channel number, facilating calibration considerably. Finally, the spectra are immediately in digital form and linear in intensity, ready for all kinds of combinations. To make CD, MCD or LD combinations however, the two kinds of spectra necessary for each should be made with alternating shots as the baseline might not be well defined. The linearity combined with the circularly polarized-light technique are the features that have made the present determination of the B3 line possible. The most severe draw-back is the lack of sensitivity of the TV videcon, which only in the infrared can compete with fast films. However, at wavelengths where films can be used, there are also image devices available with high quantum yield, which combined with a TV videcon offer the advatages of both.

CONCLUSION

It has been proven that a combination of a pulsed magnet, an optical multichannel analyzer, and the appropriate light polarizer is a powerful tool to obtain qualitative and quantitative information about magnetically active, blended absorption bands of widths up to about 100 cm^{-1}. For the magnetic field parallel to the C_3 axis, the g-factors were determined for the E^2 and $^2T_2$ states of ruby, as well as the relative intensity of the component of the $^2T_2(\bar{E}_b)$ state.

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