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Anomalous behavior of the magneto-circular photoluminescence lineshape of R_1-line in ruby (Al_2O_3 : Cr)

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MCPL spectra in the R_1-line of ruby showed an anomalous magnetic field dependence between 0.49 and 1 T, for which the level crossing occurs in the ground state ($^4A_2$) multiplet. The integrated value of the MCPL spectrum of the R_1-line showed a broad peak around 0.55 T suggesting the existence of light-induced magnetization in this material.

The magneto-circular dichroism of the absorption (MCDA) has been known to provide a sensitive tool for studies of electronic states introduced either by transition ions [1] or defects [2] in solids. The magneto-circular dichroism of the photoluminescence (MCPL) also offers the complimentary information in thin samples for which conventional MCDA measurements are difficult due to the insufficient absorption. Characterization of electronic states in transition atoms in solids by the MCPL techniques has been reported for MgO:Cr^{3+} [3] and GSGG:Cr^{3+} [4]. To our knowledge, however, no detailed reports have been published about the MCPL in ruby crystals.

The ruby (Al_2O_3 : Cr) crystals grown by the Vernouille technique were supplied from Shinkosha Ltd. The crystal was cut perpendicular to the trigonal axis of the corundum structure. The cutting was performed aligning the crystal axis by the use of X-ray Laue photography. Both surfaces were mirror-polished using the diamond paste.

The photoluminescence excitation was performed by the 488 nm line of an Ar^+ ion laser. The excitation power was less than 200 mW. The magneto-circular dichroism spectrum of the photoluminescence was measured using a piezobirefringent modulator, a Glan prism polarizer, a grating monochromator of the focal length of 250 mm, a photomultiplier and a lock-in amplifier. The MCPL, which is defined as the difference in the luminescence intensities for the left- and right-circularly polarized light was obtained as the output of the lockin amplifier tuned at the modulation-frequency component. The experimental details will be published elsewhere.

MCPL spectra of R lines in the 0.05 wt% chromium-doped crystal were measured at 25 K with several magnetic fields between 0.49 and 1.3 T. The obtained MCPL spectra of the R_1-line and the R_2-line are shown in the upper halves of figs. 1 and 2, respectively. In PL spectra Zeeman-split lines could not be fully resolved even with the highest magnetic field applied in the present study. On the contrary, a prominent structure could be resolved in MCPL spectra even with the smallest field of the measurement.

As seen in the upper half of fig. 2 the line shapes of MCPL spectra for R_2-line show no substantial variation for whole range of the magnetic fields applied. On the other hand, the MCPL line-shape of R_1-line de-

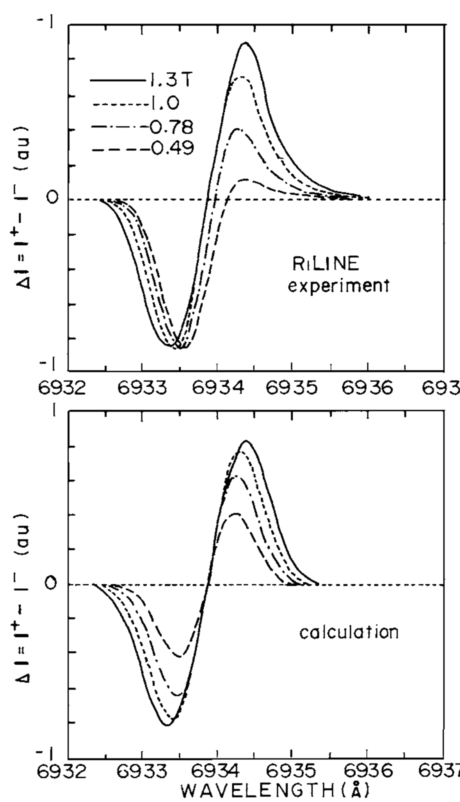

Fig. 1. Experimental MCPL spectra of R_1-line of Al_2O_3:Cr(0.05 wt%) at 25 K (upper part) and calculated MCPL lineshapes of the $\bar{E}(^2E)-{}^4A_2$ transition (lower part) at several values of magnetic field.

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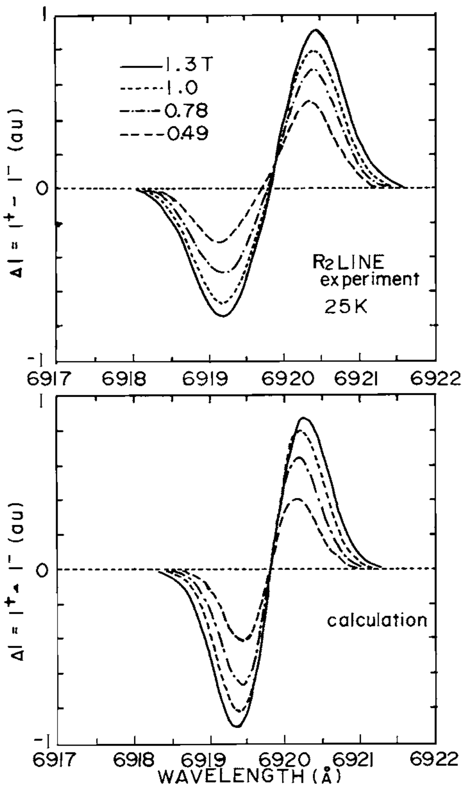

Fig. 2. Experimental MCPL spectra of R_2-line of Al_2O_3:Cr(0.05 wt%) at 25 K (upper part) and calculated MCPL lineshapes of the $2\bar{A}(^2E)-{}^4A_2$ transition (lower part) at several values of magnetic field.

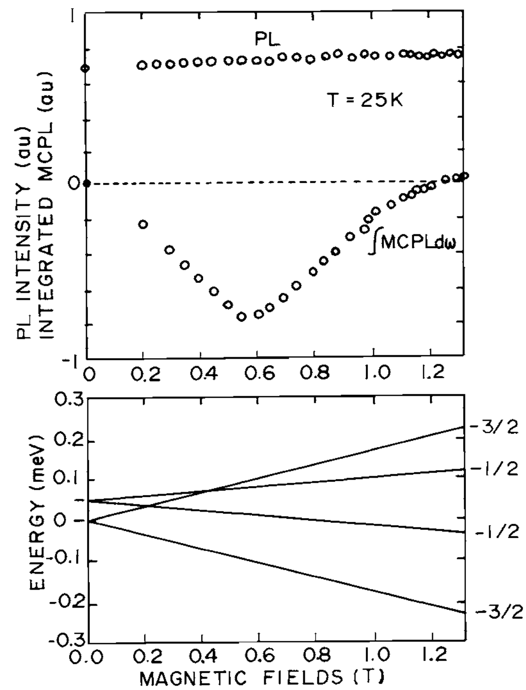

Fig. 3. The integrated lineshape (zeroth moment) of MCPL spectrum of Al_2O_3:Cr(0.05 wt%) (upper part), and the energy diagram of the Zeeman splitting in the ground state $^4A_2$.

pends strongly on the magnetic field as shown in the upper half of fig. 1. The lines shape is rather simple for the highest field applied, whereas it is very complicated for lower magnetic fields.

We evaluated the integrated intensity (the zeroth moment) of the measured MCPL spectrum of the R_1 line for each magnetic field of the measurement. The results are plotted against the magnetic field in fig. 3. The integrated intensity deviates from zero monotonously with the field up to 0.55 T where it shows a peak and then approaches to zero for higher fields. It should be noted that crossing between the Zeeman-split levels occurs in the ground state manifold in the vicinity of the field of the peak as shown in the lower half of fig. 3.

The MCDA spectrum of the R_1-line was also measured. The line shape of the MCDA was found quite identical to that of the MCPL for each magnetic field. This indicates that the anomalous MCPL shape does not arise from the strong excitation by the laser nor from the effect of re-absorption of the emission but is inherent to the electronic structure of the chromium ion in the ruby crystal.

The R_1 and R_2 photoluminescence lines have been assigned to the transitions from $2\bar{A}(^2E)$ to $^4A_2$ and that from $\bar{E}(^2E)$ to $^4A_2$, respectively. The transition matrix elements calculated by Sugano et al. [5] are

Table 1
Transition matrix elements [5]

^2E	$2\bar{A}$		$\bar{E}$	
$^4A_2$	$M_s'=1/2\ u_+$	$M'=-1/2\ u_-$	$M_s'=-1/2\ u_+$	$M'=1/2\ u_-$
3/2	$\pi/2$			$\sigma_+/2$
1/2	$\sigma_+/3$	$\sigma_+/6$	$\pi/6$	$\sigma_-/3$
−1/2	$\sigma_-/6$	$\sigma_-/3$	$\sigma_+/3$	$\pi/6$
−3/2		$\pi/2$	$\sigma_-/2$	

given in table 1. In the present configuration only the transitions denoted as σ_+ and σ_- are responsible. The ground multiplet $^4A_2$ is subject to the zero-field splitting δ_0. The magnetic field dependence of the ground state levels due to the Zeeman splitting is given in the lower half of the fig. 3. The g-value of the ground state is assumed to be 1.98. Level crossings of the $|+3/2\rangle$ state with the $|-1/2\rangle$ and the $|+1/2\rangle$ states occur at the magnetic field of 0.21 T and 0.41 T, respectively. We also assume g-values for the excited state as 2.42 and 1.46 for $\bar{E}$ and $2\bar{A}$ states, respectively, and the Boltzmann distribution of population among the levels in the calculation of the transition probability at the finite temperature. The line shape was simulated assuming the Gaussian distribution function. The line width for the Gaussian function was determined so as the observed line shape of the photoluminescence could be reproduced.

The MCPL line shapes of the R_1-line thus calculated are presented in the lower half of fig. 1, showing a symmetrical dispersion type spectrum, which cannot account for the asymmetrical features of the experimental spectra for whole range of the magnetic field considered. On the other hand, Simulated MCPL spectra of the R_2-line are in good agreement with experimental spectra as shown in the lower half of fig. 2. Such a simple behavior may be related with the fact that no level crossing occurs in the R_2-transition since the $|\pm 3/2\rangle$ states are not involved as seen in table 1.

Integrated MCPL intensity for the R_1-line was also calculated. At finite temperatures the integrated intensity varies monotonously with the magnetic field due to the population difference between transitions caused by the Boltzmann distribution. This result cannot explain the experimental magnetic field dependence of the integrated intensity shown in fig. 3, which shows a peak at the intermediate magnetic field.

It is generally accepted that in nonmagnetic materials the zeroth moment of the magnetooptical line shape of a transition from the nondegenerate ground state does not change by the magnetic perturbation [6]. Our experimental data, therefore, suggests the presence of a magnetization for the intermediate magnetic field strength. This reminds us the fact that the optically induced magnetization was observed in ruby crystals with the external magnetic field of 0.207 and 0.414 T, at which the level crossing occurs in the ground $^4A_2$ levels [7]. Another possibility can be postulated for the origin of the anomalous lineshape; i.e. this effect is caused by mixing of the $|+3/2\rangle$ and the $|+1/2\rangle$ states due to deviation from the ideal local symmetry at the Cr^{3+} ion caused by some kind of atomic disorder often observed in the Vernouille-grown crystal. Similar experiment in the flux-grown crystal is planned as future studies.

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