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Magnetic Field Dependence of Magnetocircular Photoluminescence Spectra in Ruby

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Spectra of the magnetocircular photoluminescence (MCPL) as well as the magnetocircular dichroism of absorption (MCDA) were measured in single crystals of ruby with various chromium concentrations at about 25 K. Dispersion-type MCPL structures were observed for both R_1 and R_2 photoluminescence (PL) lines.

Lineshapes of MCPL spectra of R_2-line for various magnetic fields were quite symmetrical, which could be reproduced by a theoretical calculation using the matrix elements reported by Sugano *et al.* On the other hand, the MCPL spectra of the R_1-line were asymmetric and could not be explained by the calculation. The MCPL lineshapes of R_1 were strongly dependent on the magnetic field B. The integrated intensity of the R_1 MCPL spectrum was found to have a finite value taking a maximum around $B=0.5$ T.

[magnetocircular dichroism, magnetocircular photoluminescence, Al_2O_3:Cr, ligand field transition, R-lines, N_2-line]

§1. Introduction

Magnetocircular dichroism of absorption (MCDA) has been known to provide a sensitive tool for studies of localized electronic states of transition ions in solids. One of the authors (K. S.) has been working with MCDA of transition atoms in GaAs:Cr, by which it has been proved that the method is very much effective in the characterization of Cr centers in the semiconductor.[1,2] However, MCDA measurements usually require a sufficiently thick sample to assure an appreciable absorption intensity. To observe MCDA in thin samples in which only a little absorption is expected, we can use MCPL (magnetocircular photoluminescence) instead of conventional MCDA measurements. Characterization of electronic states in transition atoms in solids by the MCPL techniques have been reported on MgO:Cr^{3+}[3] and $Gd_3Sc_2Ga_3O_{12}$ (GSGG): Cr^{3+}.[4]

However, to our knowledge no detailed reports have been published on the magnetocircular dichroism at low temperatures in ruby crystals, only exception being MCDA of the B-line in ruby by Aoyagi *et al.*[5] and room-temperature measurement of MCPL of R-line by Morita.[6]

We constructed an MCPL apparatus employing a piezobirefringent modulator and an Ar^+-ion laser for photoluminescence excitation. Using this apparatus we measured the MCPL spectra in single crystals of ruby. We made the analysis on the lineshape of the R-lines according to the ligand-field theory.[7] However, the analysis was unable to explain an anomalous magnetic-field dependence of MCPL lineshape of R_1.[8] We also evaluated MCDA spectra for wide range of photon energies.

§2. Experimental

Single crystals of ruby, Al_2O_3:Cr grown by the Vernouille technique were supplied from Shinkosha Ltd. The nominal chromium concentrations of the samples were 0.05 and 1 at%. These crystals were cut perpendicular to the trigonal (C_3) axis of the corundum structure. The cutting was performed aligning the

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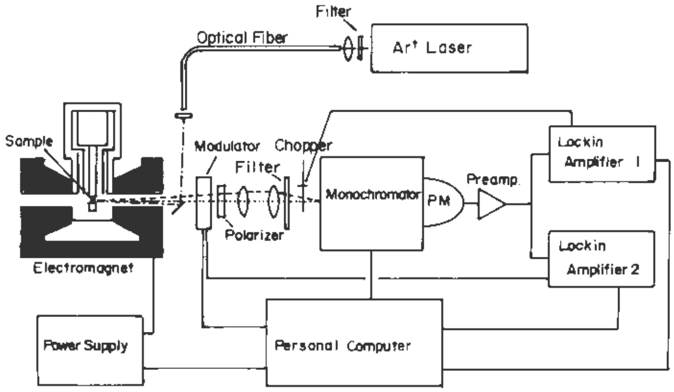


Fig. 1. Schematic diagram of measuring apparatus of MCPL.

crystal axis by X-ray Laue photography. Both surfaces were mirror-polished using the diamond paste.

Figure 1 illustrates an apparatus used for the magnetocircular photoluminescence (MCPL) measurements. The samples were set on the cold finger of the He-refrigerator cryostat inserted between the pole-pieces of the electromagnet with perforation through them and cooled down to about 25 K. Magnetic field B up to 1.3 T was applied parallel to the C_3 axis of the crystals.

We employed the 488 nm line of an Ar^+ ion laser as a photoluminescence (PL) excitation source, with the power of 100 mW.

The laser beam was focused by a small mirror placed in front of the hole of the pole-piece, on the crystal surface from which the PL emission was collected.

The luminescent emission going out through the hole at the pole-piece was collected by a lens. The light was transmitted through a piezobirefringent modulator (Hinds International Inc. Type PEM-CF3) followed by a linear polarizer. The analyzed light was lead to a JASCO CT-25A grating monochromator and detected by a photomultiplier (Hamamatsu R928). The output signal of the photomultiplier is amplified by a lockin amplifier.

A circularly polarized light emitted from the ruby crystal in the magnetic field was converted into an amplitude-modulated light with the phase determined by the sense of circular polarization.

To avoid the ambiguity in the wavelength scan of the monochromator, the wavelength scanner was driven step by step using a command from a personal computer and the MCPL signals for both plus and minus polarities of magnetic field, as well as the signal of the PL intensity at the zero magnetic field was recorded at each step. Data were averaged for 100 to 10000 repeated measurements at each wavelength. The wavelength was calibrated with the peak position of R-emission of ruby, which can be determined precisely for any temperatures using reported values.[9]

Spectra of magnetocircular dichroism of absorption (MCDA) were measured using a halogen-tungsten lamp as a white light source, the beam of which was led to the sample from the back and the light transmitted through the sample was modulated and detected as in the MCPL measurement system.

Photoluminescence excitation spectrum of the R-line was measured using a superhigh-pressure Xe-lamp as a light-source combined with the same monochromator. We used a JASCO CT-25C monochromator and the same photomultiplier for detection of the luminescence. No correction was performed for the spectral distribution of the excitation light.

§3. Results and Discussion

3.1 *Photoluminescence*

Figure 2 illustrates photoluminescence (PL) spectra of three crystals with chromium con-

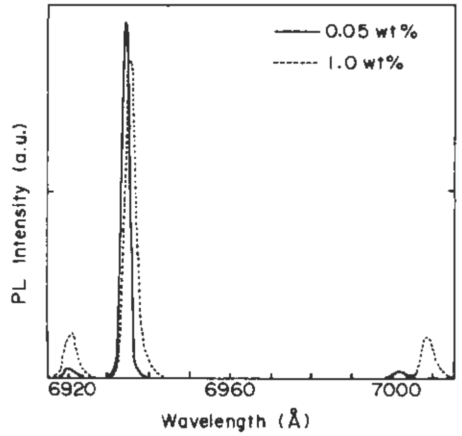


Fig. 2. PL spectra of ruby crystals with chromium concentration of 0.05 and 1.0 at% measured at 25 K.

centrations of 0.05 at% and 1 at% in the wavelength region between 6915 Å and 7015 Å at 25 K. The lines at 6919 Å and 6934 Å have been known as R_1 and R_2, respectively. An additional peak is observed at 7009 Å in samples with high Cr-concentration, which has been named as a N_2 line and believed to be caused by the Cr-pair.[10] The relative PL intensities among two samples are not so accurate in this figure, because the conditions of measurement are slightly different for each run.

3.2 MCPL spectra of R_1 and R_2 lines in 0.05 at% Cr-doped crystal

Magnetocircular photoluminescence (MCPL) spectra of R lines in the 0.05 at% chromium-doped crystal were measured at 25 K under several magnetic fields from 0.49 to 1.3 T. The obtained spectra of the R_1-line and the R_2-line are shown in Fig. 3 and Fig. 4, respectively. In the upper part of each figure we present photoluminescence (PL) spectra of the same crystal measured with the magnetic field $B=0$ and 1.3 T. Zeeman-split lines were not fully resolved with the highest magnetic field applied in the present study. On the contrary, a prominent structure could be observed even at the small field as 0.5 T.

As seen in Fig. 4 the MCPL lineshapes of R_2-line are common for whole range of the magnetic fields, showing a typical symmetrical dispersion-type spectrum. On the other hand, the MCPL lineshape of R_1-line depends strongly on the magnetic field as seen in Fig. 3. The lineshape becomes simple in the highest field applied, whereas it is not simple in the intermediate magnetic fields.

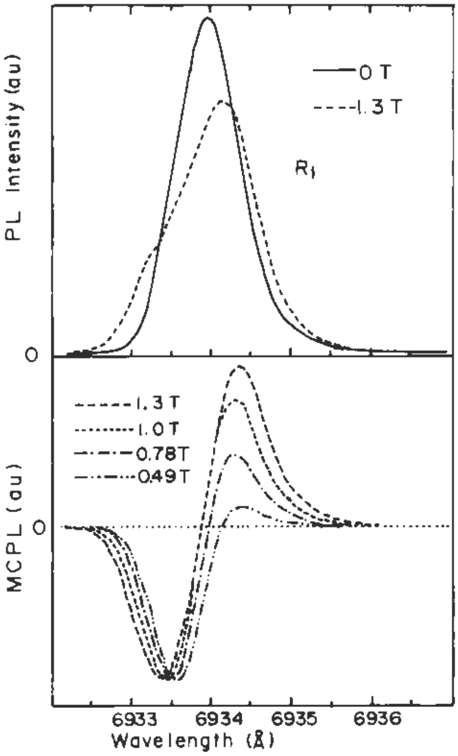


Fig. 3. PL (upper half) and MCPL (lower half) spectra of R_1-line in a 0.05 at%Cr-doped Al_2O_3 crystal at 25 K for several values of magnetic field.

3.3 MCDA spectra of the R_1 line in 0.05%Cr-doped Al_2O_3

Figure 5 shows spectra of magnetocircular dichroism of absorption (MCDA) in the R_1-line. The asymmetrical lineshape of the MCDA is quite similar to that of the MCPL shown in Fig. 3.

Since the MCDA is free from the reabsorption effect, the asymmetrical line-shape in magnetocircular dichroism cannot be correlated with the reabsorption at least for 0.05 at% Cr-doped sample.

Even in the case where MCDA measurement is possible, we can show advantages of the MCPL measurement: The MCPL experiments are easier than MCDA, because the high resolution measurement with a narrow

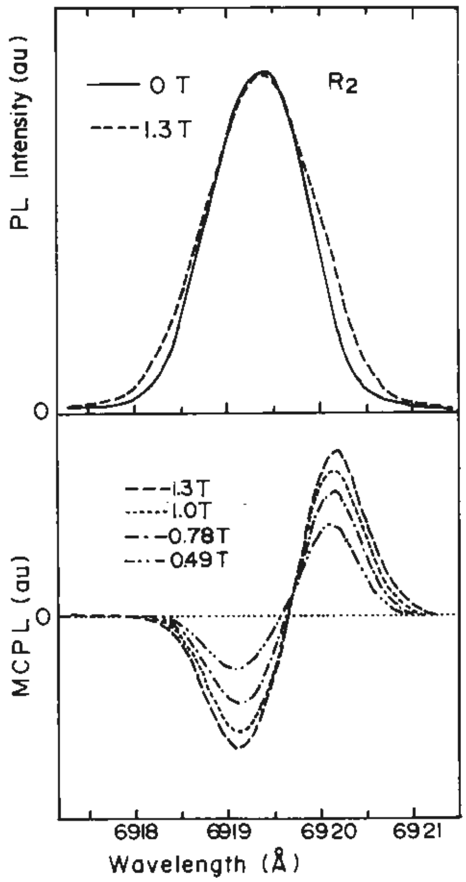


Fig. 4. PL (upper half) and MCPL (lower half) spectra of R_2-line in a 0.05 at%Cr-doped Al_2O_3 crystal at 25 K for several values of magnetic field.

slit width reduces the light intensity. Now that we have confirmed the similarity of the spectral shape between MCPL and MCDA, we can employ MCPL spectrum as easier way of magneto-optical measurement in the further investigation.

3.4 *Magnetic field dependence of the integrated MCPL of R_1-line*

We calculated the integrated value (the zeroth moment) of the MCPL spectrum of the R_1 line for each magnetic field of the measurement. The results are plotted against the magnetic field in Fig. 6 together with the integrated PL intensity. The integrated MCPL deviates from zero to the negative side as the field increases until it takes an extremum around 0.55 T. Then it approaches zero as the magnetic field reaches at 1 T.

We only remind the fact that in the intermediate magnetic field the level crossing between the Zeeman-split levels occurs as shown in Fig. 8, which will be explained in §3.5.

3.5 *Simulation of MCPL spectra using the ligand-field theory*

In Figs. 7(a) and 7(b) we give an energy diagram related to R-line transitions of Cr^{3+} under the magnetic field along the C_3 axis of the corundum structure. The R_1 and R_2 photoluminescence lines have been associated with the transitions from $\bar{E}$ (^2E) to $^4A_2$ and that from $2\bar{A}$ (^2E) to $^4A_2$, respectively.

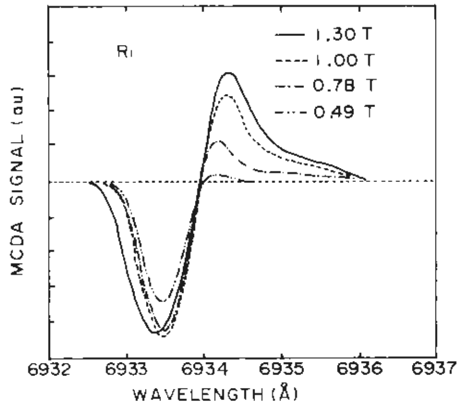


Fig. 5. MCDA spectra of R_1-line in a 0.05 at%Cr-doped Al_2O_3 crystal at 25 K for several values of magnetic field.

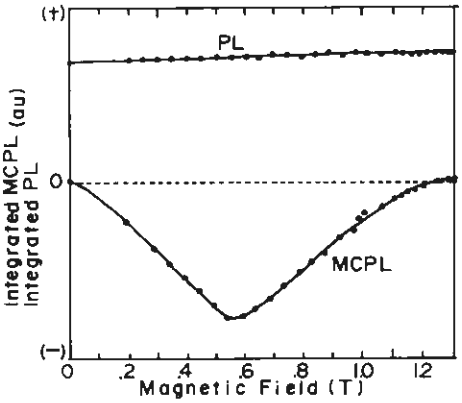


Fig. 6. Magnetic-field dependence of the integrated PL-intensity and the integrated MCPL spectra of R_1-line in a 0.05 at%Cr-doped Al_2O_3.

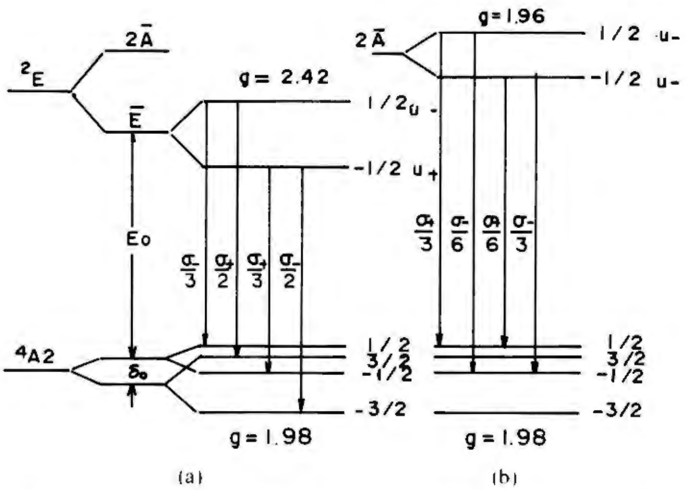


Fig. 7. Energy level diagram of the 3d^3 state in Cr^{3+} ion in trigonal crystal-field with radiative transition probabilities associated with the R-lines under magnetic field. (a) R_1 line and (b) R_2 line.

The transition matrix elements calculated by Sugano *et al.*[8] are given in Table I. In the present configuration only the transitions denoted as σ_+ and σ_- are considered. 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 Fig. 8. The *g*-value of the ground state is assumed to be 1.98. Level crossings between $|+3/2\rangle$ and $|+1/2\rangle$ or $|-1/2\rangle$ occur at the magnetic field of 0.2 T and 0.4 T.

We took into account the Boltzmann distribution of electrons among the levels in the calculation of the transition probability at the finite temperature. For luminescence transition population distribution in the excited manifold should be considered. However, since the temperature of 25 K used in the present study is equivalent to 2 meV and the Zeeman splitting of excited doublet is 0.2 meV at most, the maximum population ratio of the highest to the lowest Zeeman-split levels is 0.90. The ratio approaches unity for low magnetic field. Therefore, the asymmetry observed in the low magnetic field cannot be attributed to the population difference. This will be shown in the following.

The lineshape was simulated assuming the Gaussian function, the linewidth of which was determined so as the observed lineshape of the photoluminescence (PL) could be reproduced.

3.5.1 *Simulated MCPL lineshape of the R_1 transition*

The PL lineshapes of the R_1-line simulated for various values of the magnetic field are illustrated in Fig. 9. This provides a quite

Table I. Transition matrix elements between ground states $^4A_2$ and excited multiplets ^2E ($2\bar{A}$ and $\bar{E}$) for R_2 and R_1 emissions.

^2E M', γ' / $^4A_2$ M	$2\bar{A}$		$\bar{E}$	
	$1/2\ u_+$	$-1/2\ u_-$	$-1/2\ u_+$	$1/2\ u_-$
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		$\pi/2$	$\sigma_-/2$	

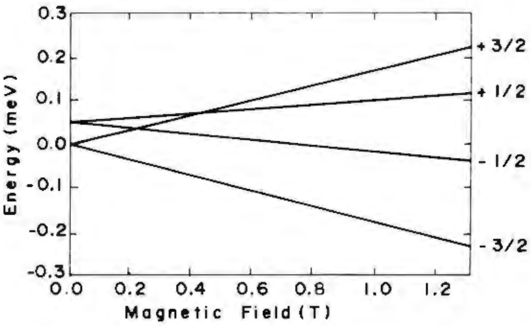


Fig. 8. Zeeman splitting of the $^4A_2$ ground state of the Cr^{3+} ion in trigonal crystal-field.

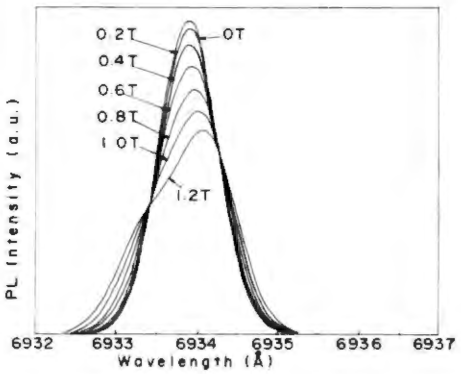


Fig. 9. Simulated PL spectra of R_1-line for several magnitudes of magnetic fields.

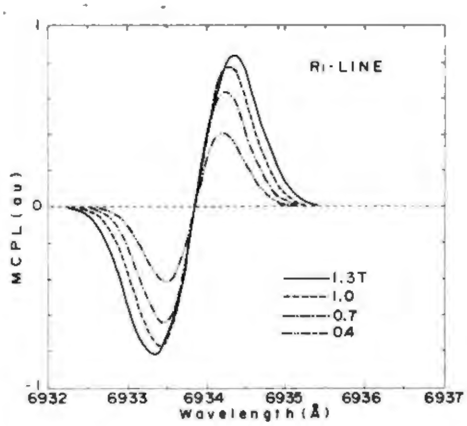


Fig. 10. Simulated MCPL spectra of R_1-line for several magnitudes of magnetic fields.

satisfactory reproduction of the experimental spectra shown in the upper half of Fig. 3. On the other hand, concerning the MCPL lineshape, the simulation provided a quite symmetrical dispersion type spectrum as shown in Fig. 10, which could not account for the asymmetrical feature of the experiment for whole range of the magnetic field considered.

3.5.2 Simulated MCPL lineshape of the R_2 transition

The simulated R_2-line is given in Fig. 11. This gives a quite satisfactory explanation of the experimental lineshape shown in Fig. 4. This agreement may be related with the fact that the $|3/2\rangle$ states are not involved in the transition of R_2 so that spectra are subject to no level crossings unlike the R_1-line transition.

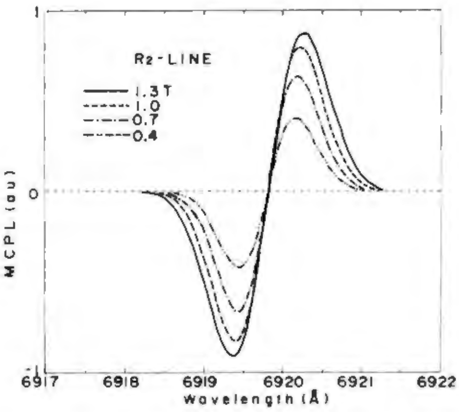


Fig. 11. Simulated MCPL spectra of R_2-line for several magnitudes of magnetic fields.

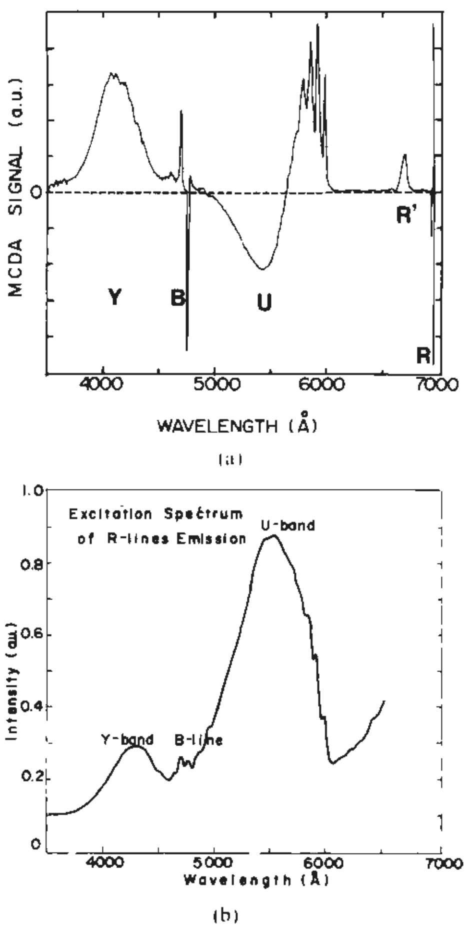
3.5.3 Integrated MCPL intensity

Integrated MCPL intensity for the R_1 line was also calculated. However, the calculated intensity varies only monotonously with the magnetic field due to the population difference among the excited Zeeman levels caused by the Boltzmann distribution.

This result could not explain the experimental magnetic-field dependence of the integrated intensity showing a convex-shape field dependence as illustrated in Fig. 6.

It is generally accepted that an integrated intensity of a magnetooptical spectrum associated with a certain transition vanishes as far as the material shows no magnetic order and the orbital angular momentum is completely quenched in the ground state.

The present experimental results therefore suggests either the presence of a magnetic order or the incomplete quenching of the orbital angular momentum. The fact that integrated MCPL takes a maximum at an intermediate magnetic field reminds us that the optically-induced magnetization (inverse Faraday effect) of ruby was observed with the external magnetic field of 0.207 and 0.414 T, at which the level crossing occurs.[11] However, since we observe the anomalous MCD lineshape regardless of laser intensity, the presence of optically induced magnetization seems less probable as a cause of the asymmetrical lineshape than the survival of orbital angular momentum in the ground state manifold.



(a)

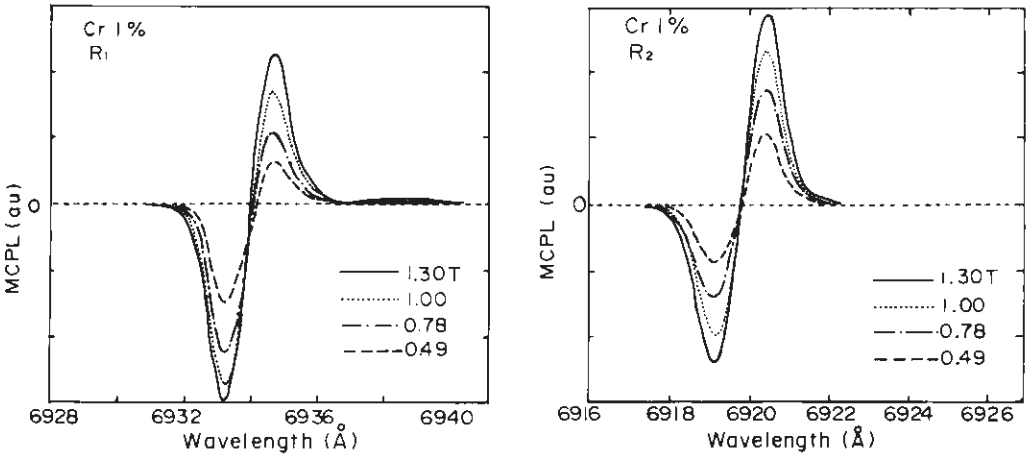
(b)

Fig. 12. (a) MCDA spectrum and (b) PL excitation spectrum of R_1-line luminescence in 0.05 at%Cr-doped Al_2O_3 crystal for wide spectral range at 25 K.

3.6 *MCDA spectra in a wide spectral range*

In Fig. 12(a) we show a spectrum of magnetocircular dichroism of absorption (MCDA) for the wide range of photon energies covering the R-line (^2E), the R′-line ($^2T_1$), the U-band ($^4T_2$), the B-line ($^2T_2$), and Y-bands ($^4T_1$). The temperature of measurement was 25 K and the magnetic field was 1.3 T. For comparison, we present an photoluminescence excitation spectrum of the R-line emissions measured at 25 K in Fig. 12(b), showing the U-band, the B-line and the Y-band absorptions, which is essentially the same as the absorption spectrum reported by McClure.[12] By comparing the two figures, we find that the MCDA line-shapes are by no means "symmetrical" for each ligand-field absorption.

The MCDA of the R′-line and the Y-band takes only positive values, while that of the U-band is composed of both positive and negative structures. For the U-band, number of MCDA structures are observed in the low energy side, corresponding to the fine structures of U-band absorption, which have been ascribed to zero-phonon line and vibronic sidebands.[13] It is found that the zeroth moment of MCDA does not vanish even for the total energy region of observation. This fact should also be taken into account in the discussion of the asymmetrical MCD lineshape of R_1-line.



(a)

(b)

Fig. 13. MCPL spectra of (a) R_1-line and (2) R_2-line emission in 1 at%Cr-doped Al_2O_3 crystal at 28 K.

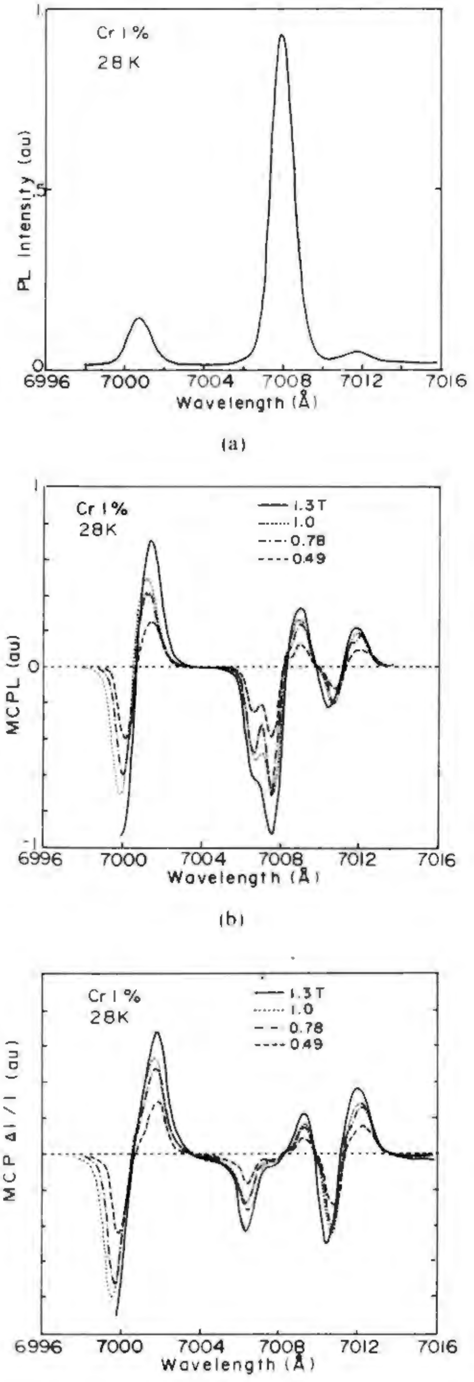
Detailed analysis of MCDA spectra will be discussed in later publication.

3.7 *PL and MCPL spectra in heavily doped sample*

In heavily-doped crystals, R-lines become broader and additional lines such as N_2-line appear. Figures 13(a) and 13(b) present MCPL spectra in the 1 at% Cr-doped Al_2O_3 crystal for R_1- and R_2-lines, respectively. Spectral shape of R_1 is also asymmetric like in the 0.05 at% sample. In addition to the 6934 Å structure, is seen an additional structure around 6938 Å. On the other hand, the MCPL spectral shape of R_2-line is quite symmetrical as shown in Fig. 13(b). In this sample several additional PL lines are observed around 7000 Å as shown in Fig. 14(a), which was not observed in the 0.05 at% sample. The strongest line at 7008 Å has been called the N_2 line, which has been believed to arise from pairs of Cr ions.[9]

The MCPL structures associated with these PL lines are presented in Fig. 14(b). The strongest PL line at 7008 Å gives rise to only a weak MCPL structure. This can be more clearly understood when one plots the magneto-circular polarization (MCP), i.e., a ratio of the MCPL to the PL intensity. The MCP spectra are given in Fig. 14(c), in which one finds that the peak-to-peak value of MCP in the 7008 Å structure is less than that of 7000 Å structure.

This fact can easily be understood if one takes into account the fact that only a small magnetooptical effect is expected for an emission from the antiferromagnetically coupled pair, in which the net changes in the spin moments are canceled at the transition.



(a) (b) (c)

Fig. 14. (a) PL, (b) MCPL and (c) MCP spectra associated with Cr-pairs in 1 at%Cr-doped Al_2O_3 crystal at 28 K for four values of magnetic field.

§4. Conclusion

We measured magnetocircular photoluminescence (MCPL) and magnetocircular dichroism of absorption (MCDA) spectra of R-lines and pair-lines of Cr^{3+} ions in ruby crystals. The MCPL and the MCDA spectrum of 0.05 at% sample show the similar lineshape. The MCPL of the R_1 emission showed a quite asymmetrical lineshape which could not be explained by the simulation based on the simple ligand-field theory. Integrated MCPL intensity deviates from zero at the medium field, where level crossings in the ground multiplet are observed. Presence of optically induced magnetization or contribution of orbital angular momentum was suggested. On the other hand, the MCPL lineshape of the R_2-line was successfully simulated by the ligand field theory. This may be explained by the fact that the R_2-line transition is subject to no level crossings.

The MCDA lines for R′, U, B and Y transitions also showed quite asymmetrical lineshape. This result suggests that the simple ligand-field treatment is not adequate to explain the circular dichroism spectra. Theoretical approach is needed for interpretation.

The MCPL spectra in the 1 at%Cr-doped crystal was also investigated. R_1-line showed an asymmetrical MCPL lineshape similar to that in the 0.05 at% crystal. We also observed MCPL signal for the N_2-line, relative weakness of the MCPL being consistent with the assignment that it is caused by the transition in the electronic states associated with antiferromagnetically-coupled Cr-pairs.

Acknowledgment

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