Observance of Spin-Orbit Splitting of Ruby Single Crystal Photoluminescence

Joowon Kim

Intermediate Physics Experiment

Abstract—**Photoluminescence of ruby single crystal is widely researched topic in optoelectrics. In this report, temperature dependence of ruby PL spectrum is first revised. It could be shown that PL spectrum shifts towards the red when temperature increases. Also, the FWHM of the band increases as temperature increases. By adaquate fitting methods, the energy gap between R1 line and R2 line is obtained as 2.86 ± 0.04 meV. Importantly, the spin-orbit splitting effect on excited energy level could be intuitively seen in the PL spectra, near the peaks(Fig.7). We applied quadruple peak profile to refit the data, and the temperature dependence of spin-orbit splitting could be obtained in Fig.6.**

I. INTRODUCTION

The induced emission of photon by quantum excitation of electrons, called luminescence, is a considerable topic in physics and widely researched recently. Preliminary studies reported about the photoluminescence(PL) of ruby crystal, especially about its bandshift, bandwidth, and their temperature dependence[1][2]. Powell suggested debye model-based theoretical approach on bandwidth of R-lines and N-lines. Due to the thermal broadening of energy level, the ground state energy level for the excited electrons has uncertainty, causing bandwidth in PL spectra. Also the bandshift is induced by thermal shift of ground state energy. Increasing temperature led to increasing bandwidth, and shifted the peaks towards lower energy. Other than temperature dependence, Seat and Sharp were able to show strain or pressure dependence of R-lines in the spectra[3]. The experimental results showed that strain has weak, inversely proportional dependence to R-lineshift.

When describing electron transition, in most general case, selection rule in quantum mechanics enters the scene and forbids certain types of transition which total spin is not conserved, for instance, singlet to triplet, triplet to singlet transition of electron. However, the crystal field perturbation re-allows the forbidden transition, therefore spin forbidden transition can happen by external photonic stimulation[4]. The excited electron can be in either spin-up state or spin-down state, since the exitation energy spectrum is broad enough to add spin-flip energy to the exitation energy. Then the spin-orbit coupling term of electron is introduced, which breaks the spin degeneracy in excited bands. If such effect is dominant, the PL bands would split into two separate peaks, since the excited energy level has splitted into two.

In this paper, the ruby single crystal PL spectra are measured and analyzed. Firs, as most of the studies did, temperature dependent PL spectra are measured and reviewed in this report. Temperature dependent behavior of peak levels, FWHM is obtained by using adaquate fitting methods. Additionally, each experimental data of R1 and R2 lines are analyzed as double peak profile to examine the spin-orbit splitting of PL bands. The fitting result is then used to compare the theoretical splitting and the experimental result.

II. THEORETICAL BACKGROUND

A. Crystalline structure of ruby

Ruby is a Al_2O_3 hexagonal close-packed crystal doped with Cr^{3+} ion, replacing aluminum sites that has octahedral symmetry. However, the deformation caused by the replacement leads to coaxial symmetry breaking of the lattice and only leaves C_{3v} symmetry on the site. The distorted octahedral symmetry subjects a crystal field on the Cr^{3+} ion which splits up the energy of $3d$ band into two. The original excited state, $^4T_2$ states has non-radiative relaxing path to excited state with lower energy, ^2E. The distorted crystal field mentioned above split the ^2E into two bands $\bar{E}$ and $2\bar{A}$, with energy gap approximately $29\ cm^{-1}$.

B. Temperature dependence on Photoluminescence spectra

Temperature dependence of PL signal is researched in many studies, and the mostly used model to explain the phenomena is the well known Debye model. Debye model predicts the heat capacitance of a lattice proportional to cube of temperature, or equivalently the energy in fourth order of temperature.

$$\langle E \rangle = 9Nk_BT\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^3}{e^x+1}dx \qquad (1)$$
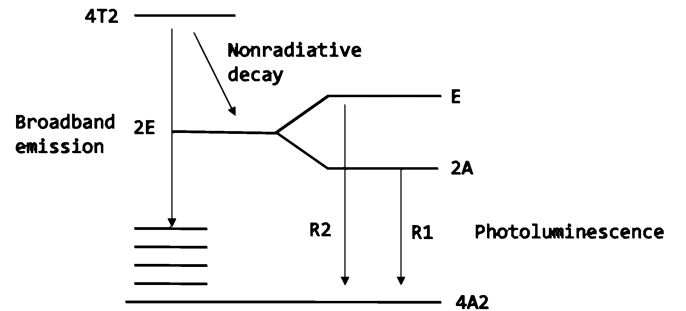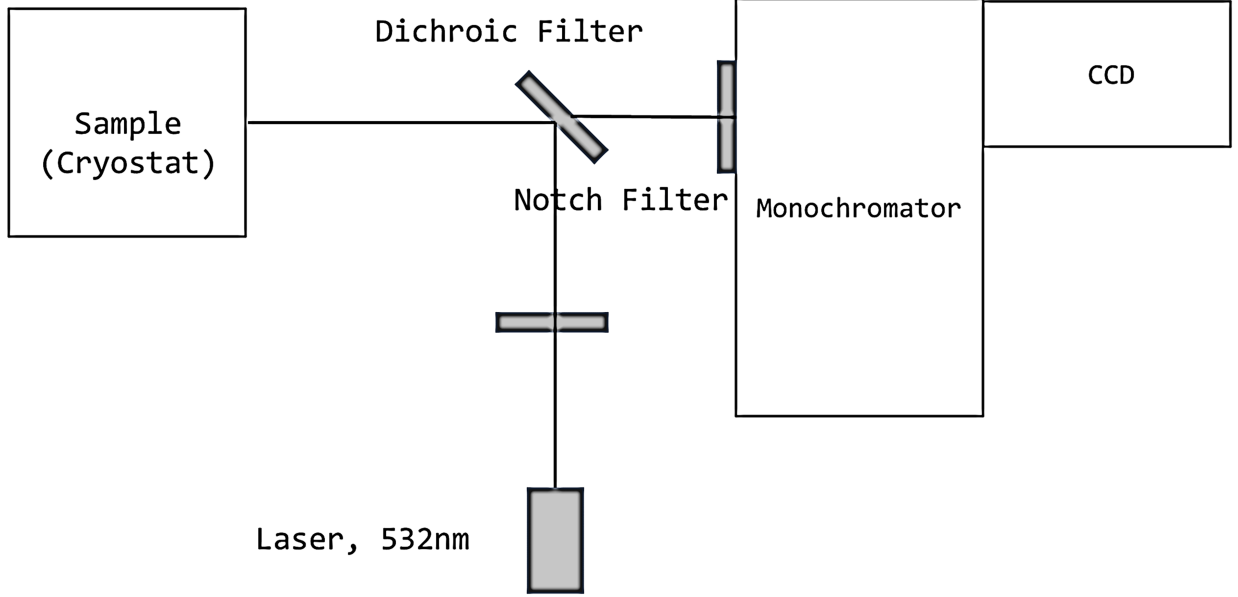

Fig. 1: Sketch of the band structure of ruby

Fig. 2: Experimental setup used for PL spectra measurement

Here, N denotes the number of total modes and T_D the debye temperature of the lattice. The integral at the end is often abbreviated as $D_3(T_D/T)$. This vibrational mode leads to the fluctuation of ground state energy since the phonon scattering enters the relaxation process. Thus the emission spectrum is shifted towards the red due to this energy dissipation process.

$$\Delta\nu = \alpha \left(\frac{T}{T_D}\right)^4 D_3\left(\frac{T_D}{T}\right) \qquad (2)$$

Where the constant α is generally negative, since the red shift is observed.

The broadening of radiative transitions have no contribution of Doppler effect, since the vibrating amplitude is small enough to fade out the large frequencies of electron(THz) and make the doppler broadening effect impotent. Moreover, experimental results from preliminary researches implies strong temperature dependence on the broadening effect, therefore thermodynamic approach to this phenomena is important. The first contribution to the broadening is direct multiphonon emission during the relaxation process[5].

$$\delta\nu_d = \sum_{j<i} \beta_{ij} \frac{e^{T_{ij}/T}}{e^{T_{ij}/T}+1} + \sum_{i<j} \beta_{ij} \frac{1}{e^{T_{ij}/T}+1} \qquad (3)$$

Where T_{ij} is defined as separation of vibrational energy divided by the boltzmann's constant, β_{ij} is a constant related to transition probability from ith level to jth level. However this term is negligible in the region of temperature our experiment was held.

The second contribution to the broadening is raman process, an inelastic scattering between electron and phonon. This term can be calculated considering electron-lattice interaction Hamiltonian, and assuming the debye statistics of vibrational mode.

$$\delta\nu_R = \delta_0 + \bar{\alpha} \left(\frac{T}{T_D}\right)^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x+1)^2} dx \qquad (4)$$

This is the term mainly considered in this report, the experimental result of FWHM of PL bands is fitted based on (4).

The two-level model used to describe the PL of ruby crystal, is result of nonradiative relaxation from $^4T_2$ energy states. The lifetime of PL in ruby is relatively short compared to our characteristic measuring time of order of few tenth of seconds, but still large enough to approximate thermal equilibrium. This equilibrium approach is suggested by Seat and Sharp, namely in the paper 'quasithermodynamic equilibrium'. The population in two energy state obeys the Boltzmann statistics, thus the ratio of population in two states is given as

$$R = exp\left(-\frac{\Delta E}{k_B T}\right) \qquad (5)$$

Where ΔE is the energy gap between $\bar{E}$ and $2\bar{A}$.

III. EXPERIMENTAL

To keep the ruby in low temperature throughout the whole experiment, ruby sample was mounted on a cryostat connected to a cooler capable to control the temperature from 10K to room temperature. A rotary pump is used to vacuum the chamber during low-pressure experiment. For photonic excitation source, SLD-532-070T 532nm laser was used. Since the bandgap of heavily doped ruby is known as 695nm, the excitation energy is high enough to excite the electrons to excited states. Dichroic filter and notch filter is used to send the excitation light accurately to the sample, and filter out the original excitation source that goes into the monochromator, respectively. DM-500i Monochromator of grating rate 1200

gr/mm was used to obtain the spectrum with 12micron resolution. The final signal was detected by Andor DV-401A-FI CCD. CCD was always cooled to -35C to reduce the dark current.

PL spectrum of Rhodamine 590 sample was obtained to test out the experimental setup. After the first measurement, the cryostat was cooled down to 10K and ruby PL signal was measured at temperatures 10K 300K, with interval of 10K. The data is processed through multiple fitting methods. Double peak model for analyzing temperature dependence, and for observing spin-orbit splitting effect, quadruple peak model or double-double peaked peak model is used.

IV. RESULTS

A. Photoluminescence of Rhodamine 590

Rhodamine 590 an organic material in Rhodamine family, with highly active flourescence. Chemical equation for this material is $C_{28}H_{31}ClN_2O_3$. Because of the resonant structure of electron in this organic material, electrons can easily absorb the excitation source and make flourescent emission. The strongest absorbtion wavelength of Rhodamine 590 in aqueous solution is at 530nm, and the strongest flourescent wavelength at 560nm.[6]

I.T.Sugiarto et. al. suggested the dual-peak emission of Rhodamine 6G organic dye, the team described the PL spectrum of Rhodamine 6G with two gaussian peaks at 550nm, 602nm (no uncertainty given)[7]. Dimers, or even polymers are formed in high concentration Rhodamine solution, which alters the absorption and emission spectra. Dimer form of Rhodamine has higher emission wavelength which is suggested by Sugiarto as 602nm. Followingly, the experimental data from this report is fitted and analyzed with double gaussian peak profile. The dual-peak fitting result of Rhodamine 590 PL spectrum
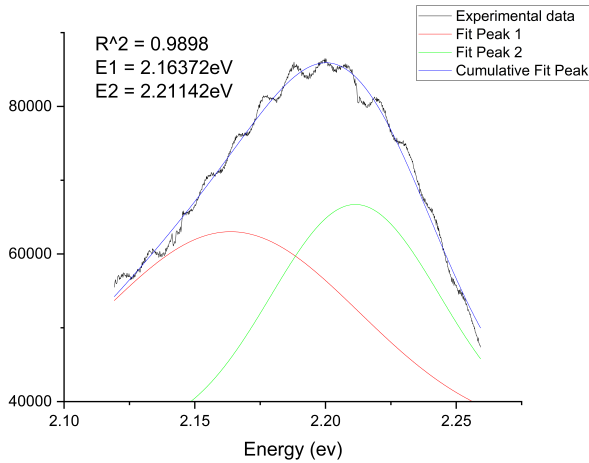

Fig. 3: PL spectrum of Rhodamine 590, at $T = 300K$(room temperature), $P = 1$atm.

is shown in Fig.3. The peak energy of two peaks are obtained as $E_1 = 2.164 \pm 0.086$ eV, $E_2 = 2.211 \pm 0.00218$ eV. Each peak energy correspondes to emitted light's wavelength, 560.76 ± 0.55nm and 572.94 ± 22.77nm. Comparing this result
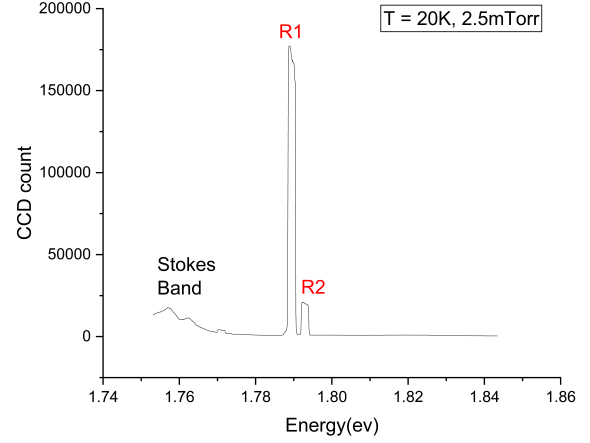

Fig. 4: Photoluminescence spectrum of ruby, at T = 20K and P = 2.5mTorr

to the data given in Ref. , the 'R1 peak' is the result of Rhodamine dimer flourescene, and the 'R2 peak' of Rhodamine monomer flourescence. The width of each peaks are 0.115 eV for the lower energy peak, and 0.0761 eV for the higher energy peak. The intensity ratio, I_1/I_2 for rhodamine spectrum is calculated as 1.34 ± 0.21.

B. Photoluminescence of Ruby Crystal

The PL spectrum of ruby single crystal is measured from low temperature(10K) to high temperature(300K). The PL spectrum showed two main peaks, which corresponds to R1 peak and R2 peak. Also, the broadband emission or Stokes emission bands are able to identify in the left(low energy) of two peaks.

The temperature dependence of bandshift, bandwidth(FWHM), intensity ratio of R1 and R2 bands, are shown in Fig.5. Figure 5A shows the temperature dependence of peak energy levels of R1 and R2 bands. Using (2), the experimental data is fitted in debye model interpretation of bandshift. The constant α_n is obtained by the fitting, $\alpha_1 = -(1.64 \pm 0.02) \times 10^{-4}$, $\alpha_2 = -(4.85 \pm 0.05) \times 10^{-4}$. The zero-temperature peak levels are obtained as $E_1 = 1.789 \pm 0.004 eV$ and $E_2 = 1.793 \pm 0.001$. The debye temperature obtained from the fitting is $692 \pm 39.0K$ and $381.3 \pm 20.6K$ for R1 and R2 bands, respectively.

Figure 5B shows the temperature dependence of bandwidth, or FWHM of R1 and R2 bands. Debye model approach is also used in analyzing and fitting the experimental data. Constants δ and $\bar{\alpha}$ are obtained from fitting. $\delta_1 = (1.64 \pm 0.06) \times 10^{-3}$, $\delta_2 = (1.63 \pm 0.03) \times 10^{-3}$, $\alpha_1 = 0.968 \pm 0.004$, $\alpha_2 = 1.120 \pm 0.006$.

Figure 5C and 5D shows the intensity ratio of two bands. Theoretical approach of 'quasithermodynamic' approximation expects this ratio to be equal to boltzmann factor:

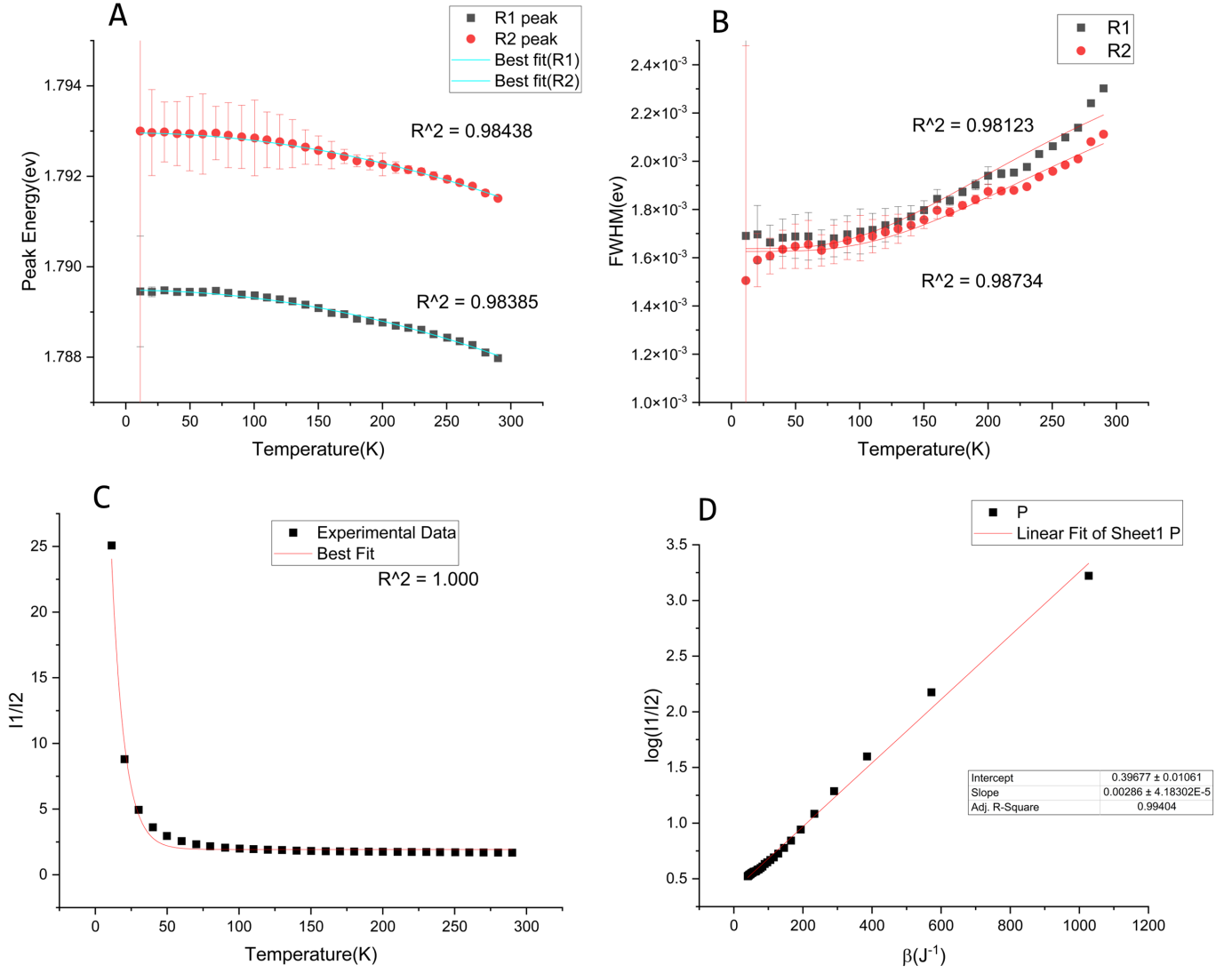$$I_1/I_2(\beta) = \exp(\beta\Delta E) \qquad (6)$$

Fig. 5: A. Temperature dependence of peak energy level, B. Temperature dependence of FWHM, C. Temperature dependence of intensity ratio, D. Linear regression on intensity ratio

β denotes $(k_B T)^{-1}$. The experimental data, in Fig. 5C is fitted in terms of (6). Also the modified data in Fig.5D, β in x-axis and $\log(I_1/I_2)$ is fitted by linear regression. The slope of the fitted function is expected to be the energy gap between $\bar{E}$ and $2\bar{A}$ state. The regression result tells the slope is $(2.86 \pm 0.04) \times 10^{-3} eV$, which is the energy gap found by experiment.

C. Spin-orbit splitting of the bands

In the previous section, experimental PL spectrum is analyzed with double voigt peak model. However, the behavior of the spectrum near the peak point, as shown in Fig.7, suggests that instead of double peak profile, fitting each peaks with two separate peaks may be necessary. This implies that the peak is splitted into two peaks, due to some internal physics. Due to allowance of spin-forbidden transition by crystal field, spin-

orbit coupling energy term enters the excited energy levels. Spin-orbit coupling energy in single atom is given by inner product of angular momentum vector and spin vector.

$$E_{SO} = \frac{2\mu_B}{\hbar m_e e c^2 r} F_r \vec{L} \cdot \vec{S} \qquad (7)$$

μ_B is the Bohr magneton, and F_r denotes the central force toward the nucleus. However, the electron here is interacting with crystal, not with a single nuclei. Therefore the equation above needs some adaquate tweaks on it. Even the lattice structure is introduced, spin-orbit terms come from the coupling of relativistic magnetic field and spin. The only term that has to be changed is the central force term. Classically, electron in a lattice does not interact with simple Coloumb potential with lattice. However the nearest atom in lattice can be always selected and the complicated force term can be approximated, assuming that the force acted on the electron, by other atoms
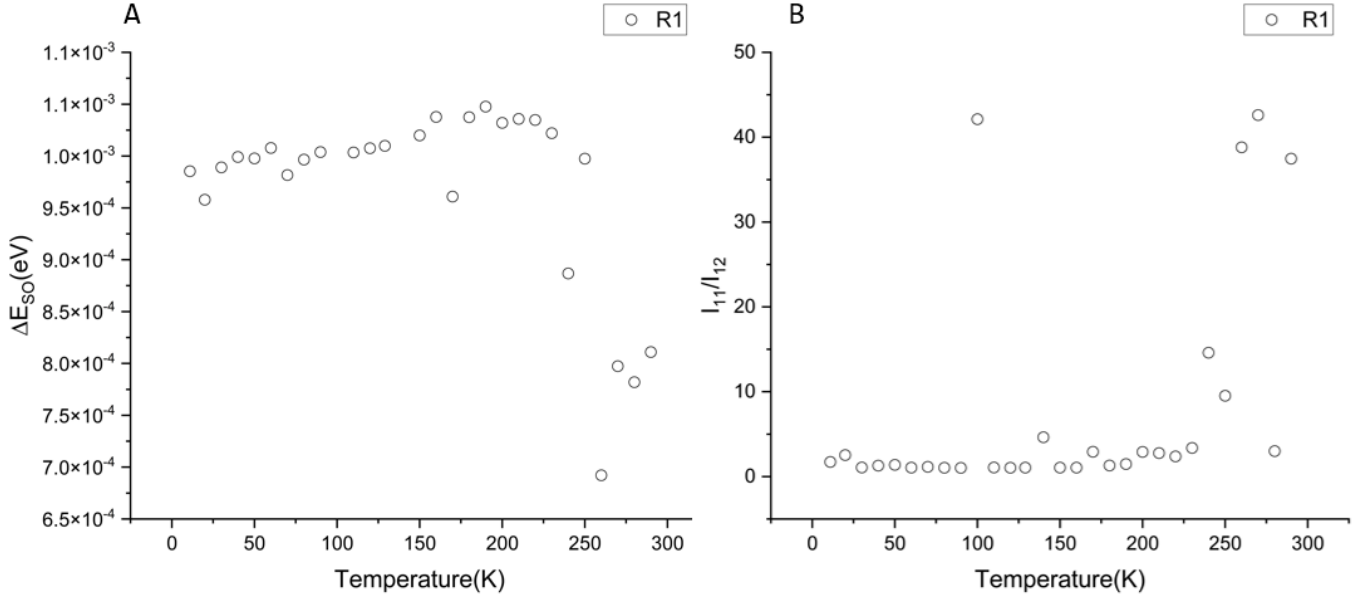
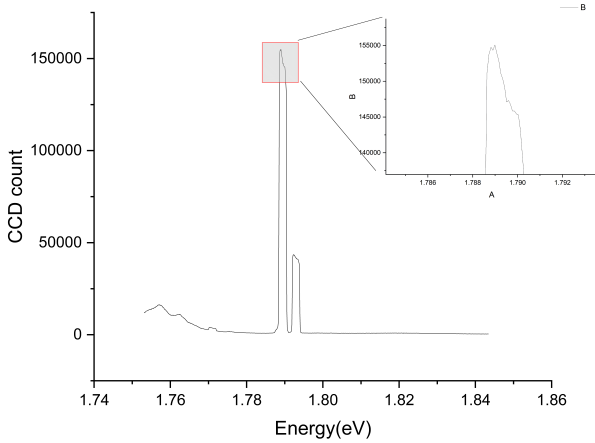Fig. 6: The Spin-Orbit splitting of PL band and its temperature dependence

Fig. 7: The double-peak behavior near the R1 peak of Ruby PL spectrum, T = 30K, P = 2.5 mTorr

in lattice is small enough to give just the screening effect. When (7) is calculated,

$$E_{SO} = Z^4 \frac{\mu_0}{8\pi} \mu_B^2 \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{n^3 a^3 \ell(\ell+1)(2\ell+1)} \quad (8)$$

In the use of assumptions above, we just consider screening effect by lattice and tweak the spin-orbit coupling term by multiplying screening constant in front of (8).

In the experiment, n and ℓ, for spin up & down electrons are the same, but j and s are the quantum numbers that matter. The energy gap caused by spin-orbit coupling is then as following.

$$\Delta E_{SO} = pZ^4 \frac{\mu_0}{4\pi} \mu_B^2 \frac{1}{n^3 a^3 (\ell+1)(2\ell+1)} \quad (9)$$

Where p is the screening constant introduced above. The 3d electrons are excited, due to chromium's valency, thus $n = 3$ and $\ell = 2$. Also the lattice constant of ruby is known as $6.64 \times 10^{-10} m$. Therefore all terms except for the screening constant can be calculated[8].

$$\Delta E_{SO} = 0.225p \quad \text{meV} \quad (10)$$

This energy gap which is dependent of spin angular momentum, splits each excited bands into two. The emission line is separated as R_{11}. R_{12}, R_{21}, R_{22}.

The peaks for every PL spectra obtained in vaious temperature, is refitted using double peak profile for each peaks. First, the energy gap between two nearby peaks, or namely ΔE_{SO} is plotted as a function of temperature. Next, the amplitude between two separated bands are plotted as a function of temperature. The first result is shown in Fig.6A, which shows that spin-orbit splitting decreases when temperature rises. The second result is shown in Fig.6. When temperature rises, especially over 250K, intensity ratio jumps and the R_{11} line dominates R_{12} line.

D. Temperature dependence on Stokes Emission

Stokes sideband emission tends to have temperature dependence, as shown in Fig.8. The intensity ratio between stokes emission and photoluminescence, is calculated for all temperature visited and plotted(Fig.9). Stokes-PL ratio shows decreasing behavior at low temperature, but increases when temperature is over certain value.

V. DISCUSSION OF THE RESULTS

The Rhodamine PL spectrum had two dominating emission peak that is fitted successfully. The intensity ratio between two peaks was obtained as 1.341 ± 0.21, which directly
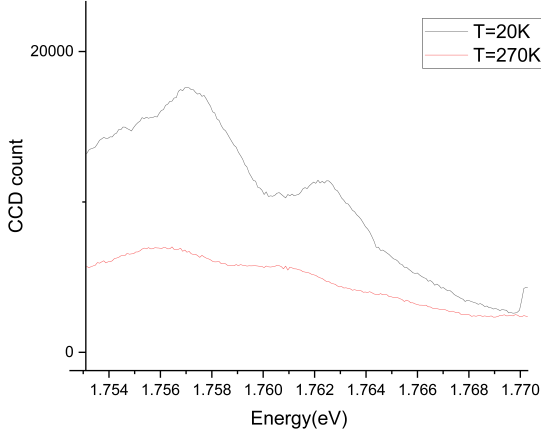
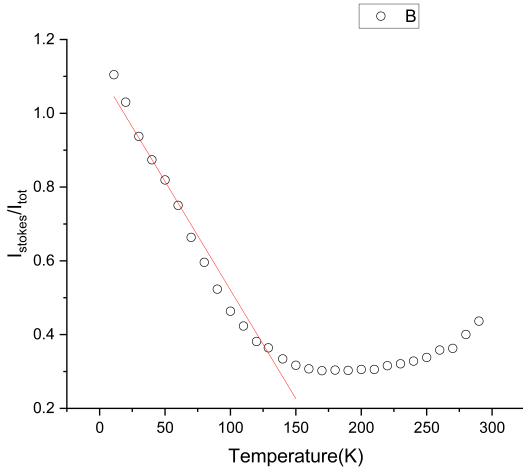Fig. 8: Stokes sideband spectrum at T=20K and T=270K

Fig. 9: Temperature dependence on Stokes-PL ratio

implies the population ratio between monomer and dimer form of Rhodamine. High concentration of rhodamine sample prepared let to dimer formation in the aqueous solution. Also, apart from the ruby PL spectrum, miscellaneous peak-like bumps are observed in the Rhodamine PL spectrum. This implies that there is more peaks lying aside the main emission peaks. Asymmetric and complicated molecular structure of Rhodamine, and existence of many covalent bonds inside the molecule leads to various splitting of degenerate energy levels. Symmetric- antisymmetric molecular orbitals split the energy level slightly, and asymmetry splits the energy level in terms of electron-nucleus interaction, with the same mechanism observed in Nuclear Magnetic Resonance(NMR). This would lead to bumpy PL spectrum of Rhodamine.

The bandshift and bandwidth of ruby PL spectrum in this report showed the expected behavior shown in previous researches. As temperature increases, the peak energy level of R1 and R2 lines is shown to decrease. Due to phonon scattering of electron, the emission energy decreases. For more precise approach to this phenomena, phonon dispersion relation of ruby lattice must be obtained and put into the integral, when calculating vibrational modes. However, to avoid cumbersome and unsolvable calculation, the Debye model was used to the analysis, which assumes linearity in dispersion relation. This might be invalid for crystal that show dispersive characteristics. The fitting resulted in high-value R-squared value, which supports that Debye model approach to the analysis is still valid enough for our Ruby crystal case.

The stokes sideband, or broadband emission should be revisited. The stokes sideband is caused by cumulative steps of indirect emission and non-radiative relaxation. For indirect emission to happen, the electrons need to stay in the indirect band for certain lifetime of the band, since the electrons nonradiatively decays to the ^2E band quickly[9]. When the temperature is low, the thermal lifetime of transition is relatively long;

$$\tau = \frac{\hbar}{k_B T} \tag{11}$$

Therefore the electrons survive longer in the indirect band. This gives more opportunity for stokes emission to happen. As a result, we could see decreasing behavior of Stokes-PL ratio in low temperature. PL is radiative and nonthermodynamic process, so has less dependence on temperature. In addition, since the relaxation time is inversely proportional to temperature, it can be easily predicted that at low temperature, the Stokes intensity will have linear behavior, which is shown in Fig.. However at high temperature, PL process is dominated by nonradiative, thermodynamic relaxation of electron in ^2E level. Increased energy of phonon makes the scattering process more probable. Therefore Stokes emission also happens in the direct band, which causes Stokes-PL ratio to rise as temperature increases.

The spin-orbit splitting of excited energy bands are observed from the PL spectra, fitted by using quadruple peak profile, and the split energy gap was calculated from the fitting result. As seen in Fig.6A, the spin-orbit splitting energy decreases as temperature rises. This can be explained using thermal effect on spin-orbit coupling. First, as temperature increases, lattice constant of ruby crystal increases in terms of thermal expansion. Since the cube of lattice constant appears in the denominator of spin-orbit term, Thermal expansion can make significant change on the splitting energy. Second, thermal process such as collision with phonon could dissipate or blur the spin-orbit coupling term, so in the process of fitting, thermal noise might have distracted the accurate fitting. While the decreasing energy gap could be explained like this, some phase transition-like behavior near $T = 250$ K needs other theory to explain. In both Fig.6A and 6B, sudden vertical jump or plunge near $T = 250$ K is observed. This critical phenomena is seemed to have connection with some kind of phase transition. Future research about spin-orbit phenomena in crystal can be a great developement of this experiment.

Apart from the energy gap, the intensity ratio between splitted energy level has significant dependency on temperature. When temperature reaches over 250K, there is a sudden jump in the intensity ratio. This could be explained in terms of lifetime of transition. Since the spin triplet state made by photonic excitation has higher energy than the singlet state

and is spin-forbidden transition, it has unstability and tends to decay towards spin singlet state. The nonradiative process happens faster when temperature goes high. Therefore in high temperature, such spin triplet state decays fast enough not to be observed in photoluminescence band, therefore makes only one state dominate the spectrum.

VI. Conclusion

By the measurement of photoluminescence spectrum, the band gap of ruby crystal is obtained. The temperature dependence of peak variables are reviewed, and they all obeyed the expected behavior. Peak bandshift was towards the left in increasing temperature, in terms of debye excitation of vibrational modes. Peak bandwidth increased as the temperature rised. The double peaked properties of each R1 and R2 lines implied spin-orbit splitting of energy levels. The result was refitted with to obtained the spin-orbit energy gap.

The future developement of this experiment would be in the high temperature region. The experiment was held in temperature $10K$ $300K$, but the diminishing of flourescence happens at high temperature region, higher than 400K. Measuring the dependence on ruby dope rate would be considerable topic as well.

VII. Reference

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