

F4

Investigation of properties of chromium in ruby and garnet

The aim of the exercise is to measure the basic properties of the chromium ion inside the cubic lattice, including: absorption, luminescence and luminescence excitation spectra at room temperature and in liquid nitrogen. Based on the measurements, individual intra-center transitions should be identified and their shift as a function of temperature determined.

1. What you should know before experiment?

1. General knowledge of solid state physics: [1, 2].
 - a) Crystal structure and band model, band structure $E(k)$.
 - b) Lattice oscillations, phonons, phonon dispersion.
2. Optical properties: [1, 2, 3, 4]
 - a) Absorption mechanisms and their ranges.
 - b) Recombination mechanisms, luminescence.
 - c) Selection rules for optical transitions.
3. Deep defects. Crystal field theory [1, 2]
4. Basic information about optical measurements [5]:
 - a) Principles of operation and construction of a monochromator,
 - b) Basis of CCD detector and camera.

It is advised to read the text below and to understand and widen your knowledge on words written in bold letters.

Ruby ($\text{Al}_2\text{O}_3:\text{Cr}$) is a variety of the mineral corundum, Al_2O_3 , doped with chromium. Pure corundum is transparent to visible light and UV to 9 eV energy. Ruby, thanks to the admixture of Cr, has a red color and other optical properties that made it widely used in the production of lasers. The measurement of the R-line shift is used to determine the pressure in diamond chambers (up to 100,000 atmospheres).

YAG - yttrium-aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$, does not occur in nature. YAG:Cr crystals that are in our laboratory were grown in ITME (Institute of Electronic Materials Technology) in Warsaw. YAG crystals are used in optics and laser production. Pure YAG crystal is colorless and with chromium is green.

The cloud of valence electrons surrounding the atom is described by a wave function that can correspond to several well-defined energies.

In the case of Cr^{3+} ion, the valence shell has the $3d^3$ configuration. State 4F is the ground state, 4P i 2G are excited states (we use here **spectroscopic notation**, the "X" record means the state with multiplicity n and symmetry X).

Dopands ions have small radii (for example Cr^{3+} radius is 1.3 Å) and when they are inside crystal, field generated by surrounding ions (ligands) can be treated as perturbation. This perturbation leads to level splitting by **crystal field**. Since chromium surroundings in ruby has octahedral **symmetry** (O_h), Cr wave functions have symmetries A_1 , A_2 , E, T_1 or T_2 .

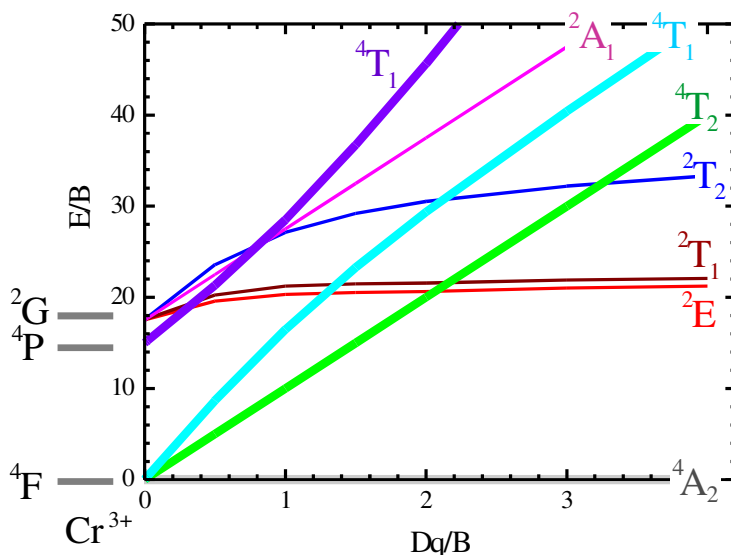


Fig. 1. Simplified Tanabe-Sugano diagram showing Cr^{3+} level splitting.

<http://wwwchem.uwimona.edu.jm:1104/courses/Tanabe-Sugano/TanSugd3.html>

The impact of the crystal field can be parameterized via the Dq/B ratio (Dq - crystal field splitting, B - electron interaction energy). Energy graph of individual levels as function of the crystal field is called **Tanabe – Sugano diagram** (see Fig. 1). The intensity of the crystal field depends on the crystal in which the Cr^{3+} ion is

immersed. In our case, the simplest relation can be observed between the splitting parameter Dq , and energy of the ${}^4T_2 \rightarrow {}^4A_2$ transition:

$$E({}^4T_2) = 10 Dq. \quad (1.1)$$

The diagram allows comparing of the similar states in different crystals and also for the given crystal in different temperatures. While crystal is cooled, inter-atomic distances shrink, influence of the crystal field is stronger and the states shift in the diagram to the left. Additionally we need to take into account influence of lattice oscillations (**phonons**). Ion - phonon interaction leads to the **line broadening** and generation of phonon replicas of electronic transitions.

Light is an electromagnetic wave, propagating according to **Maxwell's equations**. In the material medium, the speed of the wave decreases. The reflection of light is associated with the phenomenon of changing the speed of waves at the border of the media. In the absence of absorption, the reflectance, R , is given by:

$$R = \frac{(n-1)^2}{(n+1)^2}, \quad (1.2)$$

If the medium absorbs energy, the intensity of the wave propagating along the axis z , $I(z)$, decays in accordance with the formula:

$$I(z) = I(0)\exp(-\alpha z), \quad (1.3)$$

where α is **absorption coefficient**. The α dependence on the wavelength, frequency or energy of photons is called the absorption spectrum.

Absorption of the photon causes the electron transition to the excited state, for example: ${}^4A_2 \rightarrow {}^4T_2$. The excited electron can fall into the basic state emitting light in a spontaneous (luminescence) or forced (in lasers) transition. For example, line R_1 that is used in lasers this is the ruby transition: ${}^2E \rightarrow {}^4A_2$. Spontaneous emission excited by light is photoluminescence (electrically excited – electroluminescence, etc.). The strength of absorption and luminescence depends on **selection rules**. The most important rules are based on symmetries and multiplicities of the initial and final states.

Electron can relax to lower level (example: ${}^4T_2 \rightarrow {}^2E$) transferring energy to lattice oscillations (**phonons**) and then it emits photon from the. In general, the energy of the emitted photon is smaller than the energy of the absorbed photon.

Electron transitions can be coupled with ion and crystal oscillations. We then observe oscillatory lines **or phonon replicas**. If the electronic transition is accompanied by phonon emission (or transition to a higher oscillatory level), the photon emitted will have less energy and in addition to the main emission line, we will observe a peak sequence or emission band with lower energy. At high temperatures, the electron transition is sometimes accompanied by absorption of the phonon (or transition to a lower oscillatory level). Then the photon emitted has higher energy.

In the case of emission spectra, we generally observe bands with energy lower than the energy of the baseline (zero-phonon). In the case of absorption spectra, we generally observe bands with energy higher than the energy of the baseline (zero-phonon), such as shown in Fig. 2.

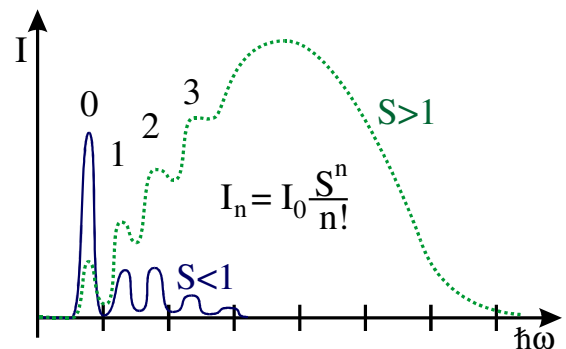


Fig. 2. Absorption spectra containing phonon replicas (S – Huang-Rhys factor).

2. The course of the exercise

- Preparation of the computerized spectrometer system: setting exposure time and reading of the background spectrum. The exposure time should be selected in such a way that the CCD camera registers can be fully used. Repeat these steps before each subsequent measurement.
- Measurements of ruby and garnet photoluminescence (PL) spectra.
- Measurements of ruby and garnet absorption spectra.
- Points B and C are repeated on a sample placed in a cryostat in liquid nitrogen.
- Measurements of the PL excitation (PLE) spectra for the R line of ruby and garnet. Spectral range 400 - 640 nm, every 10 - 15 nm.
- Analysis of the obtained spectra.

3. Report preparation

Report should be composed of the following parts:

1. Abstract,
2. Theoretical introduction,
3. Description of the measurement system and samples,
4. Results and their analysis,
5. Summary containing conclusions.

Ad. 1. The summary should be short (a few sentences), but it should contain a description of the experiences and the most important results and conclusions.

Ad. 2. It is important to introduce diagram of quantum states and explain notation (e.g. symmetries and multiplicity), allowed and forbidden transitions, etc. The most important equations and their explanation used should be provided.

Ad. 3. In the description of the system, drawings should be present.

Ad. 4. As the results of the measurements we get transmission (absorption) spectra, luminescence and luminescence stimulation spectra (PLE). Assuming that for $\lambda = 750$ nm the absorption is zero, we correct results for reflection and geometry factor, and calculate the spectrum of the absorption coefficient $\alpha(\lambda)$ from the equation (1.3).

Identify the transitions and describe the lines. Determine the R line splitting. Determine the peak shifts with temperature by comparing the spectra measured at the temperature of liquid nitrogen and room temperature. For the R line, the exact position determination of the peak requires the Lorentz curve fitting:

$$I(E) = \frac{\beta \Gamma / 2}{(E - E_0)^2 + (\Gamma / 2)^2}, \quad (3.1)$$

where: E_0 – position, Γ – width a β – height of the peak.

Discuss the temperature-induced changes based on the Tanabe-Sugano diagram and interaction with phonons (specify numerically the relations of line intensities with phonons in relation to the zero-phonon line). Determine the energy of the zero-phonon transition line ${}^4A_2 \rightarrow {}^4T_2$ in liquid nitrogen and calculate crystal field splitting Dq for Cr^{3+} in ruby and yttrium garnet (YAG) using equation (1.1).

The photoluminescence excitation spectrum should be compared with the absorption spectrum then similarities and differences should be discussed.

Ad. 5. Physical (scientific) significance of own results should be presented.

When preparing the description, remember to number equations (1) and figures (see Fig. 1). When using materials (texts, drawings, and programs) from other authors, a reference [1] should be placed in the text, and finally a list of cited sources (author, title, website address, etc.).

4. Literature

1. Neil W. Ashcroft, David N. Mermin, "Solid State Physics"
2. C. Kittel - „Introduction to Solid State Physics.”
3. T. S. Moss - „Optical properties of semiconductors”
4. G. F. Imbush - „Energy levels and transitions of transition metal ions in solids"
5. Wikipedia: monochromator, CCD camera.

K.K., 19 XII 2019