Historical remarks on the birth of the ligand field diagrams and the advent of laser

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Abstract. Tanabe and Sugano’s personal accounts are given for the birth of the Tanabe-Sugano diagrams and the advent of laser.

1. Introduction
The first laser was operated on May 16, 1960, by T. H. Maiman, using ruby (Al₂O₃ crystal Cr³⁺ impurities doped) R-line [1]. The R-line corresponds to the transitions between ⁴A₂ and ²E states in Fig. 1. For this achievement, energy diagrams of d electrons in the ligand field calculated by Y. Tanabe and S. Sugano (Tanabe-Sugano diagrams [2]) played a pivotal role. Their calculation was not meant to be utilized for the development of lasers; Tanabe did it for pure scientific interest since he was fascinated by the beautiful Racah’s method; Sugano was also fascinated by the Racah’s method, however he seemed to have an inspiration that some practical application might arise from their calculation. In this paper, a brief account is given how the calculation of the Tanabe-Sugano diagram was started, and how it contributed to the advent of laser.

2. The Confirmation of Validity
The validity of the ligand field theory was confirmed by studying optical transitions between the terms with the same orbital configurations. In the diagram, where the ground level is taken as the horizontal coordinate axis, the excited terms with the same orbital configuration as that of the ground term are almost parallel to the horizontal axis. This means that the transition energies are independent of the magnitude of a cubic crystal-field. Tanabe and Sugano noticed that optical transitions of these excited terms should be observed experimentally as a group of relatively sharp spectral lines. Actually, coexistence of such sharp spectral lines without orbital excitations and broad absorption bands with orbital excitation is the important result derived from the energy levels diagram in the ligand-field theory (or the Tanabe-Sugano diagarm) [2].

In ruby sharp spectral lines are observed as optical transitions between terms with orbital configuration t₃². These transitions of ruby are shown as R, R', and B in Fig. 1, where lift of Kramers degeneracy at right numerical figures are completely neglected [5].

2.1. Optical Studies of Transitions
It was in the nineteen-fifties that the crystal field theory of H. Bethe proposed in 1929 was applied, for the first time, to highly excited states such as those optically excited states of d-
Figure 1. Left: The Tanabe-Sugano diagram for the d^3 system [2]. Middle: The absorption spectrum of ruby [3]. Right: The energy level diagram of ruby [4]. Note that in the Figs. 5.1-5.7 of Ref. [2], d_ε and d_γ should be read as t_2 and e, respectively, in the present article.

electron compounds, though the theory has been applied to low excited states where magnetic and thermal properties are discussed.

We now show that the extended theory of Bethe, called ligand-field theory may be applied to highly excited states up to \( \sim 5 \) eV. In Fig. 2, the observed absorption spectrum of optically pumped ruby in the \( t_2^3 \) state by T. Kushida is compared with calculated one [6].

2.2. Fine Structure Spectral Line

In order to make detailed assignment of a group of sharp spectral lines coming from the transitions without orbital excitation, we have to study fine-structure of the terms caused by crystal fields of low symmetries, caused by application of external electric (Stark effect) and external magnetic fields (Zeeman effect). The best example of these transitions are found in ruby. In Fig. 2, the observed Zeeman pattern of the R1 and R2 absorption lines of ruby is compared with the theory [7, 8]; Pseudo-Stark splitting \( \Delta \gamma \) of the R-lines of ruby are also compared [9].
Figure 2. Left: The observed absorption spectrum of optically pumped ruby in the t\textsuperscript{2} state by T. Kushida [6]. Middle: The observed Zeeman pattern of the R1 and R2 absorption lines of ruby at 20 K for a magnetic field parallel to the trigonal axis and the polarization perpendicular to it [7, 8]. Right: Pseudo-Stark splitting $\Delta \gamma$ of the R-lines of ruby vs applied electric field $E_0$; Data are obtained from the R1(•) and R2(×) lines [9].

3. At Bell Labs
Sugano stayed in Bell Labs from September 1959 to August 1961, and associated with A. Schawlow, D. Wood and W. Kaiser. His host was A. Liehr.

In September 1959, at the 1st quantum electronic conference, Schawlow talked about ruby as a possible laser medium; however, he dismissed pink ruby because its three-level system would require drastically depleting the ground-state population and also because its fluorescence efficiency was then believed to be low [10].

Sugano knew that the pink ruby’s fluorescence efficiency is high through the communication with G. Kuwabara and A. Misu. He told about this to Liehr, then, his association with Schawlow, Wood, and Kaiser started. But somehow the high fluorescence efficiency of the pink ruby did not reach Schawlow.

But Schawlow and coworkers F. Varsanyi and Wood found in December 1959 that pink ruby actually has a high fluorescence efficiency. In June 1960 a paper by Maiman also reported that he had seen partial ground state depletion under flash-lamp excitation in pink ruby [1].

4. Epilog
Tanabe recalled that he never thought that laser was possible in the ruby which he have been so familiar and is an expert on it; however, retrospectively, it is totally incomprehensible why such a possibility did not come to his mind.

Sugano was impressed by the paper by Schawlow and Townes on the possibility of the optical maser [11]; however, he felt that the ruby could be used for the laser emission from association with experimentalists dealing with ruby. As seen in Fig. 1 of Ref. [5], the longest wavelength photoemission from ruby is very strong.

Anyway, things like this (even you are next to a big discovery you do not realize it and miss it) happen very often in reality; but we can say that what you are studying is more fundamental, it will more likely lead to discoveries that are of very good use [12].
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