De-excitation Processes of Optically Excited *F* Centers
Part II

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Abstract

This is the last half of the lecture note which was read at the NATO Advanced Study Institute, Erice, Italy, June 16-30, 1991. Continueing from the Part I, experimental results of the linear polarization spectrum P of the resonant secondary radiation (RSR) of *F* centers are presented. The theoretical works by Hizhnyakov, Kayanuma, and Muramatsu and Nasu to explain both intensity and P sepctrum of the RSR have been reviewed together with the generalized theory of the RSR.

3.2) Linear polarization spectrum P of the RSR.

The linear polarization spectrum P of the HL for *F* centers in KCl can be calculated from Eq. (2) using experimental data of $G_{\parallel}$ and $G_{\perp}$. It is plotted in Fig. 3 as a function of the Stokes shift wavenumber of $(\Omega_0-\Omega_2)$. The spectrum P and $G_{\parallel}$ for *F* centers in RbCl are also shown in Fig. 6 (a) and (b) [3]. These spectra were observed in our

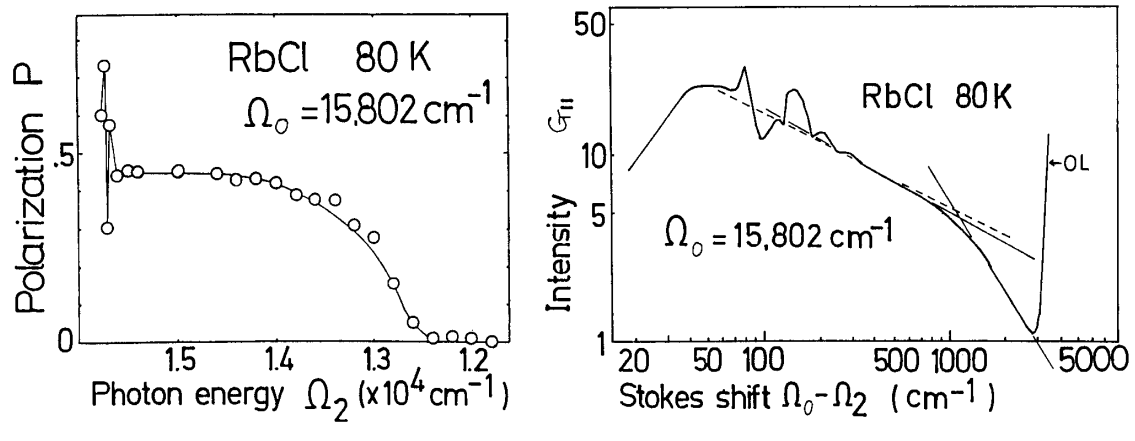

Fig. 6 (a) The linear polarization spectrum P (Ω_2), and (b) the log-log plot of the shape function spectrum $G_{\parallel}$ (Ω_2) are plotted as a function of $(\Omega_0-\Omega_2)$ for *F* centers in RbCl. Two solid lines in (b) give the gradient $n=0.58$ and $n=0.83$, respctively, when $G_{\parallel} \propto (\Omega_0-\Omega_2)^{-n}$. The dotted lines are the best fit curve of eq. (4). Taken from Ref. (3).

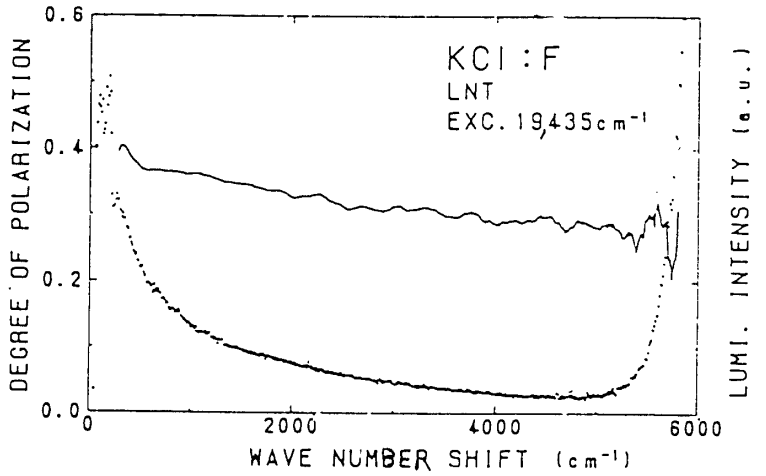

Fig. 7 The degree of linear polarization spectrum P ($\Omega_0-\Omega_2$) for *F* centers in KCl by pulse excitation is plotted as a function of ($\Omega_0-\Omega_2$). The resonant secondary radiation (RSR) intensity spectrum for F centers in KCl by *cw* excitaion is also plotted with dots. Data were taken from Ref. (5). by Y. Kondo *et al.*

laboratory with a *cw* laser exciation. Later on, Kondo *et al.* traced our results for *F* centers in KCl by means of a time-resolved spectroscopy with laser pulses from a mode-locked Ar ion laser (80MHz repetition and 0.5 *ns* FWHM) [5]. Their result of spectrum P is plotted in Fig. 7 with solid lines as a function of ($\Omega_0-\Omega_2$). The specrum G observed by them with a *cw* excitaion is shown with dots in the figure. These spectra of P and G obtained are found to be the same as ours over the whole wavenumber range except for the vicinity of the onset of the OL where the nonvanishing tendency in the specrum P was newly observed. Accordingly, they have pointed out that the polarization P is kept constant even inside the OL band region. This difference is certainly related to a merit of time-resolved spectroscopy, since, at this wavenumber region of interest, both the OL and HL could be well separated even if the OL becomes more predominant than the HL. Therefore, this discrepancy is nothing else but the difference in the excitation conditions, if considering that our *cw* excitation of *F* centers is equivalent to the pulse excitation with infinity duration time. Thus, I would claim that the physical contents described in § 3.1 would be scarcely altered. Instead, if there would be any difference, this would be a presence of a novel and unconsidered switching-off mechanism that would occur before thermlization in the lowest RES followed successively after the dynamical lattice relaxation within the adiabatic *2p*-like energy potential trough. We will discuss some detail of this problem in § 4.4.

Whatever the difference in the experimental conditions, we may classify that the whole polarization spectrum P as shown in Figs. 3 and 6 are separated into three components reflecting their characteristic dependences on ($\Omega_0-\Omega_2$). Namely, immediately after the resonant excitaion, the resonant Raman scattering (RRS) including the multiphonon resonant Raman scattering (higher order RRS) occurs in a relatively

small wavenumber range. The latter spectrum shows structureless feature becasuse of the washing out effect by phonon dispersion. As have been already reported by many authors, the RRS spectrum is characteristic in predominant peaks and large amount of reduction of P (~40%) [23~25, 32~41]. The consecutive second component is characteristic in a *gradually decreasing plateau-like depolarization* keeping a considerable amont of polarization of about 40% over the wide wavenumber range of the HL. Notice that, in § 3.1, this experimental fact has allowed us to adopt the damping oscillator model to analyze the intensity spectrum of the HL [24, 25]. The last component of the RSR spectrum is the well-known OL. Notice that the spectrum P at the vicinity of the onset of the OL is relevant to the excitation conditions as described in the preceding paragraph.

These variety of de-exciation processes of optically excited state (OES) of F centers revealed the dynamical lattice relaxation processes in a strongly coupled electron-phonon system (typically called the vibronic system). For instance, in the first range of the RRS, the intensities and its large amount of depolarization spectra observed have been already interpreted in terms of the interaction with non-cubic mode in the Fracnk-Condon state (FCS), amongst all with the predominant interaction with the Γ_5^+-mode phonon [23]. However, as was mentioned in § 3.1, the lattice relaxation in the HL range occurs in an adiabatic potential trough spanned with Γ_1^+ symmetry. This implies that the phonon interaction with non-cubic modes are much reduced in this range. Hizhnyakov particularly interesed in the depolarization mechanism at the wavenumber range from the higher-order RRS to the onset of HL [42]. According to him, the depolarization mechanism in the former is *switched off* in the latter region as a result of the Jahn-Teller splitting of the adiabatic potential energy surface in the excited electronic state. He calculated the P in a scheme where Γ_1^+, Γ_3^+, and Γ_5^+-modes interactions are taken into. However, the latter is assumed to be small so that it was treated as a first-order perturbation.

In order to explain nearly plateau-like spectral shape of the spectrum P, we have proposed that the coupling with the Γ_5^+-mode phonons could be abruptly reduced to zero at the onset of the HL just after the switching-off to the HL [4]. Buisson *et al.* had calculated theoretically the lattice dynamics in the Fracnk-Condon state (FCS), and showed that relative coupling strengths due to Γ_1^+, Γ_3^+, and Γ_5^+-modes in the F center are dependent on their orbital radius [40]. Thus, with reference to their argument, one may state that the abrupt reduction of the Γ_5^+-mode interaction is accompanied with the orbital expansion of wavefunction of excited electron [43] simultaneously at the switching-off process being the onset of HL range. We will discuss this decoupling mechanism of Γ_5^+ mode in the OES in § 4.3.

§ 4. Quantum mechanical description of the de-excitation processes of the optically excited state of *F* centers.

4.1). Review of the resonant secondary raditation

In the preceding section, we showed that the de-exciation processes of the OES of *F* centers are revealed as a consecutive series of spectrum of the HL as well as the P observed over the whole Stokes range after the resonant excitation. They are classified into three components, namely, the RRS (including the multiphonon resonant Raman scattering), the HL, and the OL separately according to the progressing of the lattice relaxation. This idea has been generally included as a second-order quantum mechanical effect entitled by *the resonant secondary radiation (RSR)* that causes the dynamical de-excition process of the OES of *F* centers coupled strongly with localized phonon systems. The concept of the RSR for the strongly coupled two-level electron system was firstly formalized by Hizhnyakov and Tehver in 1967 [44]. They derived an analytical expression of the RSR spectrum for a two-level electron system coupled with linear electron-phonon interaction, and discussed the structure of the RSR spetrum. To our best knowledge, our present measuremnt of the whole RSR specrum of *F* centers in alkali halides gave the first experimental proof for their argument [1, 2, 45].

Toyozawa gave a deep insight of the RSR spectrum and derived a general theory. He emphasized particularly the presence of the duality relation between the RRS spectrum and its time-resolved effect, based on the correlation that generally exists in complementary variables of frequency and time, according to the Fourier transform [46]. We may expect that this duality relation should be held over the whole RSR processes. Namely, the physical quantities derived from the present analysis of the RSR must be equivalent to those obtained from a ultra-fast time resolved spectroscopy. We have not heard that such a ultra-fast time-resolved measurement with as short duration time as the lattice relaxation time of 0.3 *psec* has been ever carried out over the whole Stokes range yet. One exception was the work by Savikhin, who estimated the phase relaxation time shorter than ~ 20 *fs* [47]. Thus, for the time being, our present work remined as sole experimental data to depict the RSR.

Toyozawa *et al.* derived theroetical forms of the RSR spectrum for the two cases of weak and strong coupling [48]. Above-mentioned theories belong to the generalized theory, which was often used to give a qualitative interpretation for a real system. There might be some discrepancy from the results which were derived from the conventional theory to explain all of experimental facts semi-classically. For a concrete comprehension of the real physical scheme, a new theoretical framework sould be necessarily developed so as to include the convensional theory on the basis of the generalized theory. We will call the new framework the *realizing theory*, here.

At the earlier stage in the study of the RSR for *F* centers, only a tiny part of the HL spectrum was observed in small wavenumber range from the higher order RRS [24,

25]. Hizhnyakov calculated the swithing-off effect in this wavenumber range from a viewpoint of the generalized theory. After we completed the measurement of the RSR spectrum over the whole range, two theoretical groups in Japan have given its quantum mechanical foundation on a realizing scheme. They are Kayanuma in Tohoku University [29, 30], and Muramatsu (Utsunomiya University) and Nasu (Institute for Molecular Science) [49]. Finally, Muramatsu, Aihara (Yamaguchi University) and Nasu calculated the RSR response for pulse excitation [50]. We will review briefly three theoretical works in proceeding subsections.

4.2) Switching-off effect by Hizhnyakov

As was introduced briefly in § 3.2, Hizhnyakov has studied theoretically the switching -off effect by taking into account only the *2p* state in the OES which is coupled with the phonons of Γ_1^+, Γ_3^+, and Γ_5^+-modes [32]. The switching-off effect on the degree of polarization, P, is mostly relevant to the excited photon energy over the wavenumber in the F absorption band, since it is caused by the Jahn-Teller splitting of adiabatic potential energy surface. In fact, he predicted the followings :

(1). P observed after the resonant excitation at the F band peak is smaller than that

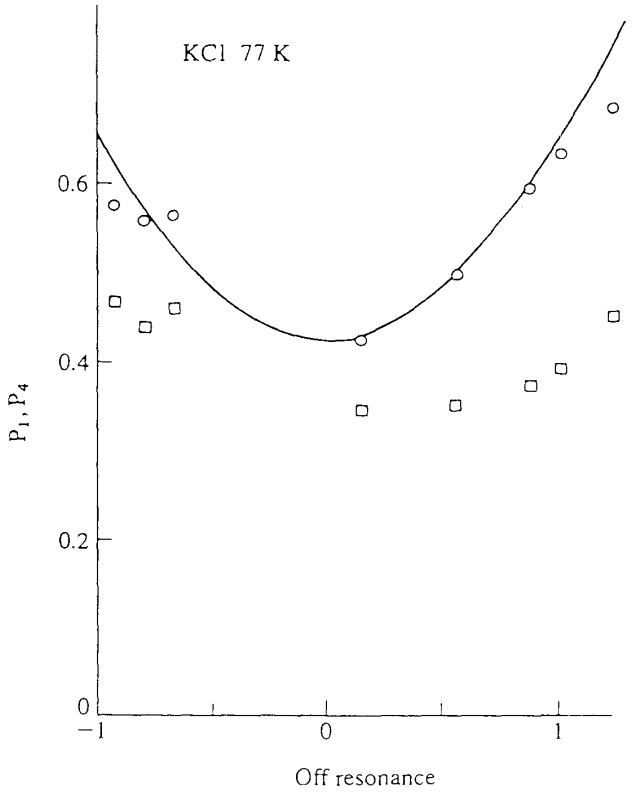

Fig. 8 The linear polarization spectrum P, where P_1 (open circles) and P_4 (open squares) are taken at the wavenumbers corresponding to $\hbar\omega_{LO}=1$ and 4 separated from the peak of the F absorption band (Ω_0), are ploted as a function of off resonance ($\Omega_0-\Omega_2$). Solid lines are from Ref. (4). Taken from Ref. (4).

excited at the lower energy tail of the F band.
(2). P observed at the beginnig range of the HL is relevant to the excitation photon energy, Ω_0, in the following manners that the P observed when excited at the lower energy tail of the F band is much larger than the P observed when excited at its high energy tail.

The items predicted are qualitatively satisfied with our experimental results as shown in Fig. 8, a part of which was taken from Fig. 3. From the theoretical curve-fitting analysis of these experimental data, Muramatsu has tentatively determined the fitting parameters, which would be a nice measure to account for the interaction strengths of coupling phonons in the FCS with certain symmetries [51]. However, they are incoincident with those determined in the FCS [23], so that they could hardly describe the real system of the OES of F centers except for giving a qualitative meaning [51]. The fact ascertains the statement in the preceding paragraph that, from fitting analysis on the basis of the generalized scheme, one cannot derive a convincible physical quantities which can describe any other physical quantities already established for describing the OES including the FCS, RES, and RSR consistently. This is a fatal charactor in the generalized scheme because it is sometimes too abstractive to describe the real physical situation of the OES. Thus, for the concrete understanding of the RRS switching-off mechanism and any other related phenomena, we must establish a new theoretial aspect in which the Hamiltonian and its solved wavefunction for the OES would be well to explain all of the observations consistently. This corresponds to the realizing theoretical scheme that was mentioned in the preceding subsection.

Fianlly, we will point out two factors that were deficient in Hizhnyakov's scheme. They are the spin-orbit interaction (Γ_4^+ symmetry) and the electron-phonon (Γ_4^- mode) interaction. Certainly, the former interaction in the FCS would be unavoidable factor since the FCS is characterized by a large negative values of the spin-orbit interaction constants [23]. Furthermore, the neglect of the latter contribution would be more unrealistic since it acts to admix the *2s* state with *2p* state. Notice that the HL occurs from one of the higher excited states of the RES, which is specified by $J=0$, where J is a total angular momentum being described in § 4.4, and is mainly composed of the admixture of *2s* and *2p* states via electron-phonon interaction [6~13]. Thus, we suspect that the Hizhnyakov's switching-off mechanism should be re-examined by taking into account two sorts of interactions cited above. Furthermore, there might be another factor to be argued. That is the anharmanicity in the adiabatic potential energy surface mentioned in § 3.1.

4.3) Kayanuma's theory for the HL intensity spectrum

Kayanuma has investigated quantitatively the features of *the intensity spectrum of RSR* (abreviated in *the RSR spectrum*) of the OES of F center in connection to the relaxation dynamics of the strong coupling system, not only its stationary but transient

response of the system [27, 28]. He assumed that the GS and OES are connected by a constant transition dipole matrix element, and proceeded the calculation of the RSR spectrum along the time-dependent formalism by Toyozawa [46]. In the four-time correlation function which appears in the generating function for the RSR, he pointed out that the pairing-off property does exist in the strong coupling system. This is an advantageous result to ascertain the validity of our classical damping oscillator model as proposed intuitively in § 3.1.

He described that, after the resonant excitaion, a wave packet of phonons is created at the FCS and it behaves like a classical damping oscillator to fall down in an adiabatic potential trough. (Notice that the electron is strongly coupled with phonons). On this scheme he calculated the RSR spectrum with adopting following parameters : They are the electronic excitation energy, $\triangle=2.313$ eV, the lattice relaxation energy divided by a representative phonon energy $\hbar\omega$ (the so-called Hang-Rhys factor)$=40$, where $\hbar\omega_{LO}=26.8$ meV and $\omega=\omega_{LO}/2$. An adjustable parameter of (γ'/ω) is left for fitting analysis, here, γ' is related to the radiative lifetime τ_r through $\tau_r=(2\gamma')^{-1}$, and $\omega\fallingdotseq(2\pi\ \tau_{LR}{}^{-1})$where τ_{LR} is the lattice relaxation time that is coincident with the quantity γ^{-1} defined in § 3.1. In Fig. 9, the experimental RSR spectrum is shown with dotted lines as a function of frequency shift $(\Omega_0-\Omega_2)$. A best fitted curve of the theoretical spectrum is plotted with solid lines. Here, a fitting parameter of 5×10^{-6} was adopted for (γ'/ω). From Fig. 9, he derived that the observed spectrum can be primarily understood as the lattice relaxation in the strong coupling system. Thus, his theory gives a semi-quantitaive agreement with experimental results. However, further detailed investigation reveals the two following anomalies which imply the real

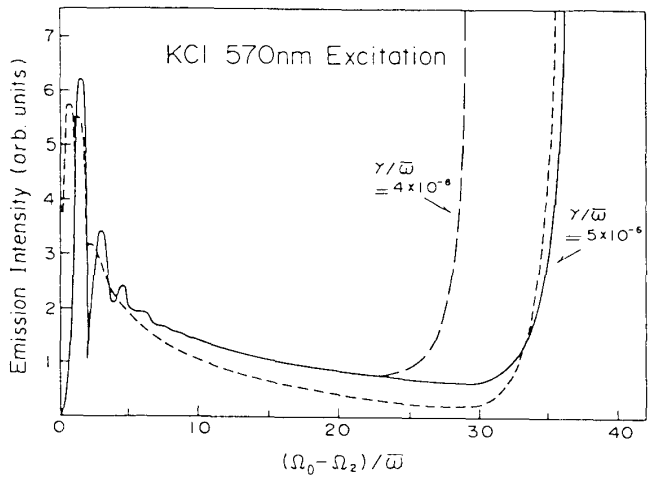

Fig. 9 The RSR spectra of the of F centers in KCl for theoretically calculated (solid lines) and the experimenatlly observed (dotted lines takedn from Ref. (1)) ones with 17240 cm^{-1} excitaion are plotted as a function of $(\Omega_0-\Omega_2)$. The broken lines are plotted when $\gamma'/\omega=4\times10^{-8}$ (see text). This figure was taken from Ref. (27) and (28) by Y. Kayanuma. Note that $\omega=\bar{\omega}$ and $\gamma'=\gamma$.

system is rather outside of the simple two-level model in the Condon approximation. 1). The tendency of decay of experimental RSR spectrum is far more steep than the theoretical curve. The discrepancy shows that the reduction of the transition probability begins at a very early stage of the lattice relaxation and goes on continuously to the RES. This idea is consistent with that described in the last paragraph in § 3.2. For a more detail, he suggests that there are two possible mechanisms giving rise to the reduction of the effective value of the transition matrix dipole moment, which have not been included in his calculation. One is the *2s-2p* level crossing during the lattice relaxation [52]. His argument is based solely on the lattice relaxation in a *2p* excited state, so that the contribution from the *2s* level is neglected. However, this contribution would not be neglected particularly at the energy range where *2s-2p* level crossing does occur. The other is the mismatching of the wave function of *2p* and *1s* states due to the enlargement of the *2p*-orbital by the polaron effect. One may expect that the drastic reduction of noncubic interactions observed just after the resonant excitation, (as discussed in § 3.2), would contribute to the reduction of the transition matrix element during the lattice relaxation. In addition to these two factors, we may also point out that the anharmonicity in the APES would give rise to the discrepancy. 2). The theory claims that the onset rise of the OL from the HL in the RSR spectrum depends on the parameter value of (γ'/ω) which gives a best fit value of 5×10^{-6}. Then, if assuming that the value of τ_{LR} to be as 0.3 *ps* as was already determined in § 3.1, we may estimate a value of τ_r to be about 10^{-8}sec, which is anomalously small in comparison with τ_r in the RES that was 6×10^{-7}sec observed experimentally [53]. Longer τ_r gives Smaller value of (γ'/ω). This leads to shift the onset rise of OL to higher wavenumbers than that observed. As an example, he plotted a theoretical RSR spectrum with broken lines in Fig. 9 setting $(\gamma'/\omega)=4\times10^{-8}$. One may find the wavenumber of the onset of OL calculated is incoincident with experimental curve. The discrepancy can be solved, if assuming that the τ_r of the OES of *F* center is reduced by a factor of 10^{-2} compared with that in the RES. This assumption would be approvable since the electron keeps mostly *2p* nature during the dynamical lattice relaxation process. In KCl, the *2s-2p* level crossing may occur near the terminal states of the OES [49]. The well-known anomaly in the radiative lifetime of the *F* center [11, 53] will happen after the thermalization in the RES.

In addition to these claims, it is regretful that the calculation of the spectrum P has not been carried out yet on this scheme. However, according to Kayaunma, this could be done easily because there is no troublesome problem left in the scheme [54]. This possibility should be tested.

Finally, his calculation predicts the enhancement of the HL at the classical turning point of the damping oscillator. He suggested that it may peak at 536 meV below the peak photon energy of the OL band [27, 28]. This may correspond to the enhanced luminescence as can be seen with bar in Fig. 5. below the OL peak.

4.4) Muramatsu and Nasu's theory for linear polarization spectrum of the RSR

In § 3.1 and § 4.3, we showed that the HL spectrum can be explained in terms of the damping motin of a classical oscillator along the APE surface spanned in the Γ_1^+ mode interaction coordinate. One more important finding is the polarization spectrum P of the HL which shows a garadually decreasing plataue-like tendency as shown in Figs. 3, 6, and 7. Muramatsu and Nasu have been interested particularly in the vibronic relaxation in the OES, and calculated it quantum mechanically. Actually, they suggested that the spectrum P observed can be treated as the depolarization processes due to *2s* ⇔ *2p* nonradiative transition which occurs during the lattice relaxation in a scheme wherein the *2s* and *2p* excited states are nearly degenerate [49]. The physical scheme can be treated in a *pseudo* Jahn-Teller system that corresponds to a vibronic scheme being mostly coupled with Γ_1^+- and Γ^{-4}-mode interactions. Based on this mechanism, they considered qualitatively that the nonradiative transition channels could occur between eigenstates of Hv_{ib} in Eq. (1) for the vibronic states of the RES. As was mentioned in § 2.1, Eq. (1) can be diagonalized already so that the OL intensity and its external perturbation effects have been well described consistently [7~13]. The energy eigenvalues are classified by a good quantum number J of total angular momentum, J being 0, 1, or 2, which correspond to Γ_1^+, Γ_4^-, and $(\Gamma_3^+ + \Gamma_5^+)$ symmetries in *Oh* field [7~10]. However, in the optical cycle of F centers, only the vibronic eigenstates *with lower angular momenta*, $J=0$ and 1, are expected to play important role, since only these states are directly related to the light absorption and the resonant secondary radiation. Based on this consideration, they have soley taken the vibronic states with $J=0$ and 1 The nonradiative transition : $|J=1> \Rightarrow |J=1>$ or $|J=0> \Rightarrow |J=0>$ with no angular momentum change occurs by releasing a Γ_1^+-phonon quantaum number from the relevant system to the reservoir through a coupling Hamiltoninan, while the transitinons $|J=0> \Rightarrow |J=1>$ with an angular momentum change occur by releasing a Γ_4^--mode phonon. They emphasize that, in a 0 K approximation, the optical transitions from the ground *1s* state occur only to the states with $J=1$, while the OL occurs from the lowest vibronic state with $J=0$, and hence the second channel contributes to the depolarization during the relaxation. They calculated the depolarization spectrum P $(\Omega_0-\Omega_2)$ modified from eq. (2) in which $I_{\parallel}$ and $I_{\perp}$ are calculated as the shape functions of HL, S_{ij} $(i, j=z, x)$, as a function of $(\Omega_0-\Omega_2)$ whose suffix z shows the polarization direction of excited light, and x shows that in the analyzer for detection. Note that S_{zz} and S_{zx} are coincident to $G_{\parallel}$ and $G_{\perp}$ in Eq. (3),respectively. They also calculated the net shape function of HL, S_t $(\Omega_0-\Omega_2)$, that is a sum of both components of S_{zz} $(\Omega_0-\Omega_2)$ and S_{zx} $(\Omega_0-\Omega_2)$. On the quantum mechanical calculation of S_{ij}, they adopted the Kayanuma's vibronic scheme of the RES [10] for the eigenvalues of Hv_{ib}. Actually, they took into upto 66th vibronic states. The calculated curves of both quantities of P and S_t are plotted with broken lines inFig. 10 (a) and (b) as a function of $(\Omega_0-\Omega_2)/\omega$. Our experimental data [1, 2] are also plotted with solid lines in the same figure. In fact, P $(\Omega_0-\Omega_2)$/P($\fallingdotseq$0) is plotted instead of P, since the Γ_3^+

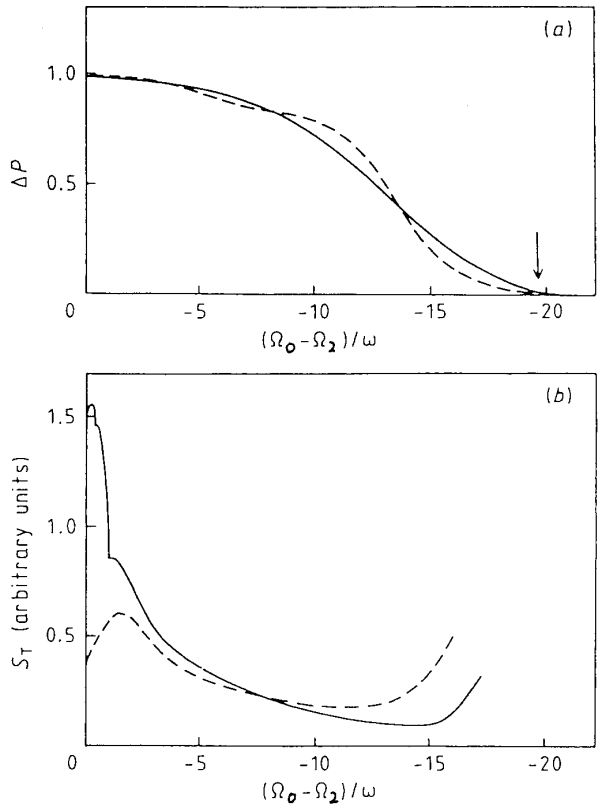

Fig. 10 The spectra of the linear plolarization (a) and the RSR (b) of *F* centers in KCl for the cases of theoretically calculated (dotted lines) and experimentally observed (solid lines taken from Ref. (1)) are plotted as a function of $(\Omega_0-\Omega_2)$. Figures were taken from Ref. (49) by S. Muramatsu and K. Nasu.

and Γ_5^+ modes which might determine the $\triangle$ P($\fallingdotseq$0) are not explicity included in this model. As for the fitting parameters, in addition to the vibronic parameters by Kayanuma [10], a relaxation rate of 0.2 $(\omega/2\pi)=1.2\times10^{12}sec^{-1}$, which is rather reasonable value, was chosen. The calculated depolarization shows characteristic features such as found in the experiment. However, the S_t $(\Omega_0-\Omega_2)$ calculated shows a single peak near the excitation energy $\Omega_2\leqq\Omega_0$, where the peak value of the S_t obtained experimentally is still larger than that calculated. The discrepancy may be related to the neglect of the contributions from the non-cubic electron phonon interaction such as Γ_3^+ and Γ_5^+ symmetries. They emphasized that this peak in the spectrum S_t is mainly constructed in terms of the contributions from the off-diagonal part of the density matrix, reflecting the character of the Raman scattering. No effort has been done to clear the discrepancy.

They expected that the dynamical relaxation due to the level crossing might occur near the level crossing of *2s* and *2p* [54]. However, no expected dynamical processes come to appear in the observation. This fact is closely related to their derived evidence

that the crossing point would be very close to the photon energy peak of the OL. The level crossing point would depend on host crystals. For instance, we proposed previously that the level crossing may occur in RbCl nearly close to the FCS [3.4]. Thus, we suspect that one may find a plasuible evidence of the dynamical relaxation caused by the level crossing in different host crystals. This experimental checking for various alkali halides is left as a future problem.

Based on the same vibronic scheme of the OES of F centers as was considered in the preceding paragraphs, Muramatsu, Aihara, and Nasu investigated theoretically the time-resolved spectrum of P and HL intensity, S_t, at a fixed Ω_1 as a fuction of $(\Omega_0-\Omega_1)$ under pulse excitation [50]. The result gives clearly the background for the distinguishing the HL and OL in the transient behavior. Unfortunately, no precise experimental study has been carried out yet.

At the first paragraph in § 3.2, we point out that the novel switcing-off mechanism, which is different from Hizhnyakov's proposal, would be possibly observable at the wavenumber region near the vicinity of the onset of the OL. This would give us detailed information on dynamical processes that may occur after the lattice relaxation in the *2p*-like adiabatic potential trough before establishing the thermal equilibrium. A preliminary measurement of the switching-off time was carried out once [55]. Result showed that it occurs within 200 *ps*, which is anomalously long time duration as was expected for the occurrence of usual thermlization. The extension of this work is under consideration in our laboratory.

§ 5. Conclusion

By means of the extensive study of the resonant secondary radiation (RSR), de-excitation processes of optically excited state (OES) of F centers in various alkali halides have been investigated as a typical example of the vibronic lattice relaxation in the OES for the localized electronic defect centers strongly coupled with phonons. The RSR consists of three components which successively appears as the resonant Raman scattering (RRS) including the higher-order RRS, the hot luminescence (HL), and the ordinary lumisescence (OL). Using a *cw* Ar ion laser or a Dye laser pumped with it for excitaion light source, we have observed the intensity and polarization spectrum of the RSR for F centers at 80 K as a function of the Stokes shift wavenumber over the whole Stokes range. We have found that the former spectrum tends to decrease smoothly until vanishing nearly at the onset of the OL, and the latter spectrum shows gradually decreasing plateau-like behavior with high polarization value of nearly 40% over the whole HL range to vanish at the onset of the OL.

We have analyzed semi-quantitatively the intensity spectrum of the HL by adopting a classical damping oscillator model that would be falling down in an adiabatic potential energy trough spanned in an interaction coordiante of Γ_1^+-mode after resonant excitation. From a theoretical curve-fitting of experimental data, the lattice relaxation time is estimated to be 0.3×10^{-13}sec.

Generalized quantum mechanical formalism of the RSR has been derived firstly by Hizhnyakov and Tehver in 1967. It has been sophisticated by Toyozawa in 1976. Hizhnyakov proposed that a switchng-off mechanism occurs at the transition wavenumber region from the higher-order RRS to the HL. He predicted a checking way of experimental proof for his general theory. Muramatsu showed that our experimental results gave qualitatively nice fitting with his prediction, and derived several parameters from the curve-fitting of experimental proofs. Although these parameters give a certain and qualitative measure for the OES, they would be scarcely meaningful to describe the physical quantities in the real system of the OES of *F* centers, particularly for the FCS. This is because they were not quantitatively related to the vibronic parameters obtained already from quantum mechanical scheme of the real system. Therefore, we would say that the switching-off mechanism has not been completely described within his theory. We need to establish the realizing theory as discussed in § 4.1, in which the realistic vibronic scheme of the FCS and RES are included as a basis of the generalized theoretical scheme.

After progressing our experiments on the RSR over the whole Stokes range, theoretical efforts to partially establish the realizing theory have been developoed by two schools in Japan ; they are Kayanuma, and Muramatsu and Nasu. In fact, Kayanuma ascertains the validiy of our classical damping oscillator model by finding the pairing-off property in the four-time correlation function in Toyozawa's generalized theory. He calculated the intensity spectrum of the RSR, in both stationary and transient situations, in the case when the lattice relaxation of *2p*-like electronic state in an adiabatic potential energy trough spanned by interaction coordiante of Γ_1^+-mode. The lattice relaxation time can be estimated to be 0.3 *ps* from the curve-fitting analysis of the over whole HL intensity spectrum, if adopting $\tau_r = 5 \times 10^{-9} sec$ being a reasonable amount of a radiative lifetime of an excited pure *2p* electronic state to a *1s* state.

On the other hand, Muramatsu and Nasu have succeded in reproducing the spectrum P of the HL by the quantum mechanical calculation based on a vibronic scheme of the OES of *F* centers which is constructed from the vibronic parameters of the RES that were determined by Kayanuma for the lowest RES of *F* centers which consists of *2s* wavefunction admixed by a small fraction of *2p* wavefunction mostly coupled with Γ_4^--mode interaction phonon [7~13, 43]. From the curve-fitting analysis, they estimated the lattice relaxation time of 0.8 *ps*.

It would be astonishing to see that these lattice relaxation times, which have been derived here indirectly from three different ways, are almost coincident each other. On the other hand, we noticed that this quantity could be determined directly from a time-resolved spectroscopy. However, nobody has ever tried it yet partly because of experimental difficulty. Therefore, for the time being, this is at least the only measure of the lattice relaxation in the OES that represents the de-exciatation processes of the OES. Lucky enough, the validity of this value is supported by the duality relation of the RSR that was derived by Toyozawa [46]. It states that the physical quantities derived

from the analysis of the spectrum of RSR would give the same quantities as could have been obtained from a ultrafast time-resolved spectroscopy method.

In spite of such a manifest success in theoretical efforts to establish the realizing scheme for describing the RSR spectrum, we claim that its achievement would be still far away from a goal. For instance, Kayanuma's theory has not been applied to explain the spectrum P yet. The application of Muramatsu and Nasu's theory to explain the HL intensity spectrum has shown poor coincidence with experimental data, particularly at the wavenumber correspondintg to the RRS region followed by the onset of HL. These difficulties are still left unresolved, so that they should be solved in a near future. We further hope that, in this realizing theoretical framework, the description of transient response could be included, so that the Hizhnyakov's switching-off mechanism and the novel swithching-off mecahnism proposed in this article should be explained automatically in the same theoretical scheme.

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