De-excitation Processes of the Optically Excited F Centers

Part I

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Abstract

This Part I consists of nearly one half of a lecture note which has been read at the NATO Advanced Study Instiute, Erice, Italy, June 16-30, 1991. The last half will apear in a subsequent issue of this periodical. In this work, the de-excitation processses of the optically excited F center has been revealed through the experimental study of the resonant secondary radiation and its linear polarization of F center in KCl. Semi-classical explanation of these findings are presented by proposing a classical damping oscillator model. The lattice relaxation time during the whole Stokes range is estimated to be 2.7×10^{-13} sec.

§ 1. Introduction

Science has often broken up a commonly accepted idea. In this talk, I will present a tiny example to have broken a common sense accepted for the investigators of luminous centers. They have thought that in the relaxation process from the optical excitation to the ordinary luminescence (OL), no luminescence would be observed. Thus, the process is called the *nonradiative process*. Its spectral range is called the Stokes range. In this lecture, we will show that the luminescence has been observed over the whole Stokes range for the F center in several sorts of alkali halides[1~4]. Our experimental data for KCl were confirmed by Kondo *et al.* using a *ps* time resolved spectroscopy[5].

The F center is an electron trapped by an anion vacancy, so that its electronic energy scheme is well approximated as a hydrogen atom. The optical processes of the F center can be dealt simply with the interaction of two-level electronic system coupled with a photon system resonantly. The adiabatic potential energies (APE) of these two levels are plotted in Fig.1 as a function of a normalized coordinate Q_l, or the interaction coordinate, Q_i, that was introduced by Inoue and Toyozawa[6]. When the F center is optically excited, the electron in the ground state (GS) is excited to the Franck Condon state (FCS), vertically at the equilibrim position Q_0, according to the Franck and Condon principle. This gives rise to absorption band. Thus-excited electron
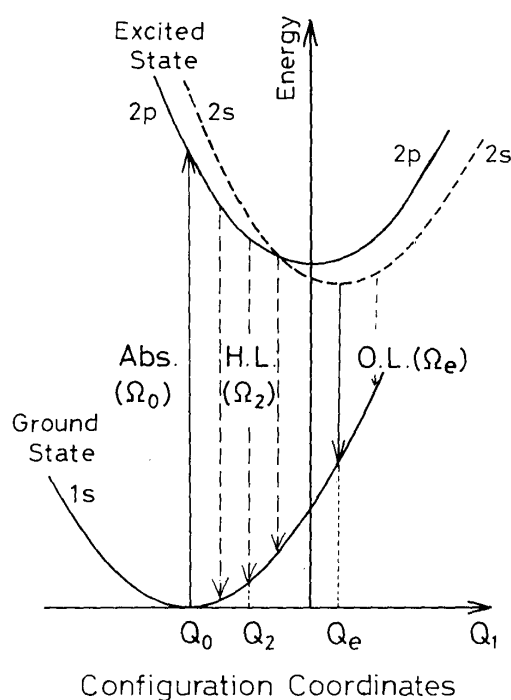
Fig. 1 Adiabatic potential energy (APE) scheme of ground and
        optically excited states of an F center is plotted as a
        function of configurational coordinates, (interaction coor-
        dinates), Q_l.

will relax down to an equilibrim position, Q_e, in the APS, which is called the relaxed
excited state (RES) being thermalized. Over the Stokes range from the FCS to the
RES, it has been so far believed that the de-excitation processes would be caused
through the emission of multi-phonons, so that no luminescence would be observable.
Thereafter, the electron at Q_e returns to the GS by emitting the OL whose photon
energy is equivalent to the vertical energy difference in the APS at Q_e.

Both absorption and OL bands observed are broad and separated by large Stokes
shift of nearly one eV. This implies that the F center can be approximated as a
well-localized two level system coupled strongly with a phonon system. Particularly, in
the optically excited state (OES) of the F center, the $2s$ and $2p$ levels are nearly
degenerate, so that the OES is apporoximated as a *pseudo Jahn-Teller system*. In other
word, the OES of the F center can be treated as a *vibronic scheme*, in which the
contribution from the vibrational and electronic states are nearly admixtured.

In this talk, we show the first evidence of luminescene observed for the F center in
KCl over whole Stokes range. Its explanation will be presented in the Part II that will
appear next issue of this periodical.

§ 2. Optically Excited State and its De-excitation Process of an F Center

(2.1) Vibronic scheme of the excited state of the F center

Ham[7], Ham and Grevschmühl[8], Kayanuma and Toyozawa[9], and Kayanuma[10] have
founded the quantum mechanical background on the vibronic scheme of the RES in the

F center, that corresponds to the lowest state of the OES. They showed that it can be described in terms of two sorts of vibronic parameters, namely, an energy difference between $2s$ and $2p$ electronic levels before introducing the vibronic interaction, Δ_{s-p}, and a coupling costant, S_i, coupled with phonons of Γ_i -mode symmetry. These values are found to be nearly equal to each other with the LO phonon energy, $\hbar\omega_{LO}$. The fact shows a characteristic property of the vibronic structure.

As a first approximation, the Hamiltonian of the vibronic structure, H_{vib}, can be written as following,

$$H_{vib} = H_e + H_L + H_{eL}, \tag{1}$$

where H_e, H_L, and H_{eL} are the Hamiltonians for pure electronic state, phonon system, and electron and phonon interaction. With reflecting the symmetry nature of H_e, that consists of nearly degenerate $2s$ and $2p$ electronic states, the symmetries of interacting phonons are confined to Γ_1^+, Γ_3^+, Γ_5^+, and Γ_4^- modes. Thus , the AEP of vibronic system can be described as a function of the interaction coordinate, which is a linear combination of a product of normalized coordiantes multiplied by a weighted fraction of coupling strength[6]. Thus, the eigenfunctions of eq. (1) can be represented by a linear combination of a product of wavefunctions of interaction-mode phonons and of electron that consists of $2s$ and $2p$ states. Actually, the vibronic state is described in terms of three quantities which are a total angular momentum J that is a sum of electron orbital angular momentum, ℓ, and the phonon ones of L, the z-component of J, M, and the number of phonons involved . By diagonalizing eq. (1), the vibronic energy scheme of the OES of F center is described with vibronic parameters of Δ_{s-p} and S_i. These parameters for the RES are determined from the external perturbation effects on the OL, particularly from curve-fitting analysis of the temperature dependences of Stark polarization[11~13], stress-induced polarization[14,15], and magnetic circular polarization[16~20] of the OL, and of the radiative lifetime of the RES[21~22]. The parameters obtained for the F centers in eight different host crystals were summarized in Ref. 22. On the other hand, the parameters in the FCS had been already determined from the external perturbation effects on the absorption via the moment method known as the HSS method. The works were mostly done in the University of Illinois[23].

When one examines carefully specific features of parametes in both FCS and RES, one may recognize that a remarkable change does occur dynamically in the Stoke range. First, the energy differences between $2s$ and $2p$ in both states have changed its signature during the de-excitation process, although their orders of magnitudes are almost the same. Secondly, the stree coupling constants in both states have shown drastic change. Namely, at the FCS, the stress coupling constant with Γ_1^+mode symmetry phonons is almost equal to the sum of other noncubic terms due to the Γ_3^+ and Γ_5^+ symmetry, where both constants are almost equal each other[23]. But, at the RES, the Γ_1^+ mode interaction predominates the other two, and the Γ_5^+ mode interaction is much reduced[14,15]. Thirdly, the spin-orbit interaction constants, which have a large negative values in the FCS, are much reduced at the RES[19,23]. This implies that,

while the electron dissipated most of its energy dynamically to the phonons, the vibronic structure itself tends to change drastically during the relaxation. On the other hand, the transition matrix elements between $2p$ and $1s$ are still kept allowed in this range. So that, we may expect that the luminescence reflecting the drastic change of vibronic scheme can be observable in the Stokes range. This is our motivation to plan to measure the luminescence over the whole Stokes range for entire comprehension of the dynamical de-excitation processes that occurs in the OES.

(2.2) Observation of hot luminescence of the F centers in KCl

In 1982, we succeeded in observing the luminescence and its linear polarization over the whole Stokes range in the 90° configuration to the incident photon flux[1]. The luminescence appears successively as the resonant Raman scattering (RRS), the hot luminescence (HL), and the OL[4]. This reveals occurrence of typical resonant secondary radiation (RSR), which will be described in coming Part 2. Their intensity is defined by $I_p(\Omega_0, \Omega_2)$ photons (energy. sec)$^{-1}$, where Ω_0 and Ω_2 are the wavenumbers of the incident (excited) and detected photons, and subscript p indicates the polarization vector of RSR either along the parallel ($\parallel$) or perpendicular ($\perp$) to the polarization of the incident light. With two observable quantities of $I_{/\!/}$ and $I_{\perp}$, we calculate the linear polarization of the HL defined as following,

$$P(\Omega_0, \Omega_2) = [I_{/\!/} - I_{\perp}]/[I_{/\!/} + I_{\perp}]. \tag{2}$$

Typical spectrum of $I_{/\!/}(\Omega_0, \Omega_2)$ and $P(\Omega_0, \Omega_2)$ in KCl at 80K are shown in Figs. 2 and 3. It shows that, after multi-phonon RRS range, the spectrum $I_{/\!/}$ decreases to zero before the onset of the OL, but the spectrum P shows a smoothly decreasing plateau-like dependence on Ω_2. Almost the same characteristics as KCl have been observed in KBr, RbCl, and RbBr[3,4]. Before accomplishing our work, measurements of HL had been
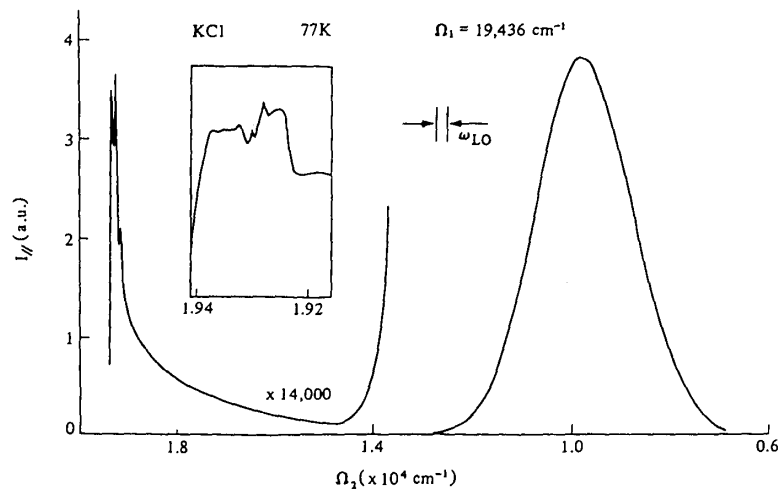

Fig. 2   The resonant secondary radiation (RSR) spetrum for F center in KCl at 80K is plotted over whole Stokes range as a function of Ω_2. It consists of the resonant Raman scattering (RRS), the hot luminescence (HL) and the ordinary luminescne (OL). The insert is an expanded figure of the RRS. Taken from Ref. (4).
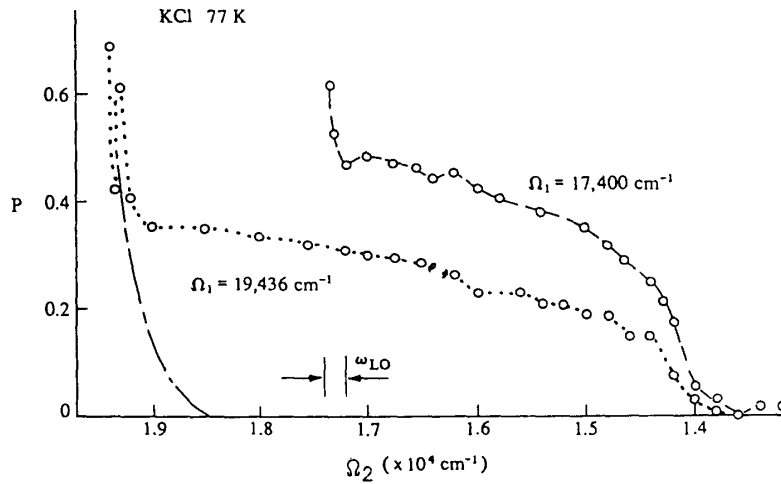
Fig. 3   Degree of linear polarization of the RSR for F center in KCl at 80K calculated
from eq. (2) is plotted as a function of Ω_2, when excited at 19, 346 and 17,000 cm^{-1}.
Taken from Ref. (4).

tried tentatively by Buchenauer et al. late in 1960's[24]. The work was follwed by Lüty's school[25]. But, they were not successful in completing the luminescence measurements over the whole Stokes range. One of the reasons of their failure in measurement would lie on the choice of sample temperatures. At LHeT that they have chosen, the luminescence spectrum was suffered from the intense emission of the F_2^+ centers which were left in the specimen. We chose sample temperature at 77K where the F_2^+ luminescence was thermally quenched completely[26]. We found that the HL in KCl is almost independent of temperature. Kondo et al. also confirmed the temperature independence of the HL below at LHeT[5]. The fact is a convincible evidence to show that the HL is continuously cooled down to the OL.

From I_p measured, one can calculate a following shape function $G_p(\Omega_0 - \Omega_2)$,

$$G_p(\Omega_0 - \Omega_2) = I_p(\Omega_0 - \Omega_2)/\Omega_2^3 \qquad (3)$$

As the G_p is proportional to the dipole matrix element of the luminous transition, eq. (3) is more advantageous than $I_p(\Omega_0 - \Omega_2)$ for the theoretical comparison. The spectrum $G_{//}$ for KCl is shown in Fig. 4[4]. In the following section, we will analyze our results semi-classically.

§ 3. Semi-classical Explanation of HL and its Liner Polarization
3.1) HL

A plateau-like dependence of the spectrum P over the whole Stokes range as shown in Fig. 3 implies that the dynamical relaxation in the OES of the F center may occur predominantly through the interaction with Γ_1^+ mode. With this implication, one may propose a mechanism of dynamical relaxation as if the excited electron could behave like a classical damping oscillator of wave-packet-like phonon, so that it could roll down to the bottom of the APE trough spanned in a one-dimentional interaction coordiante of Γ_1^+ symmetry, Q_l. Here, the motion of Q_l of the damping oscillator is

presented with a damping constant, γ, and the angular frequency of $\omega_a{}^{3,4)}$. Now, it is evident that the time duration for the electron to stay at the coordinate of Q_2 is proporional to the HL intensity with photon energy, Ω_2, and is also inversely proportional to the relaxation velocioy of damping oscillator (dQ_1/dt) at Q_2. This idea has been also verified theoretically by Kayanuma[27,28]. The shape function of HL can be calculated with a following equation except for unimportant factors,

$$G_p(\Omega_2) \propto \int (\dot{Q}_1)^{-1} \cdot \delta\{W_e(Q_1) - W_g(Q_1) - \Omega_2\} dQ_1, \qquad (4)$$

where δ is a δ-function for the energy conservation at the Q_2, W_e and W_g are the APE for the OES and GS. The W_e is described usualy by a sum of linear and quadratic variation of Q_1. In Refs. 3 and 4, we postulated to add an anharmonic term of Λ $exp(-Q_1/\rho)$ to W_e by replacing linear term, where Λ and ρ are adjustable constants. The introduction of this term gives better achievement than the previous ones for the consistent explanation of the anisotropies which were observed in both band shapes for absorption and OL of the F centers by Gebhardt and Kühnert[29].

The broken lines in Fig.4 is a fitting curve of eq. (4) with fitting parameters of (γ/ω_a) = 0.2. It is found the same amounts of fitting parameters are obtained for KBr and RbCl. This ratio shows that the oscillation period is a small fraction of the damping period, so that the damping model is rather valid. Now, we may assume reasonably that the inverse of γ corresponds to the *lattice relaxation time* of the excited F center, τ_{LR}.

Using the values of ω_a as 1.86, 1.76, and 1.60($\times 10^{13}$sec^{-1}) for KCl, KBr, and RbCl[29], the τ_{LR} for KCl, KBr and RbCl are determined as 2.7, 2.8, and 3.3×10^{-13} sec, respectively[4].

From eq. (4), we may expect that the HL will be much enhanced at the classical turning point of the damping oscillator, when $\dot{Q}_1 = 0$. From Fig. 1, and considering γ/ω_a = *0.2*, we may predict that the enhancement of HL will be observed at lower energy
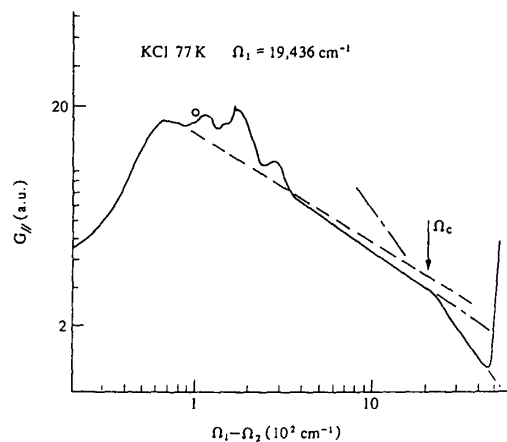

Fig. 4 $G_{//}$ calculated from Fig.2 using eq. (3) is plotted as a function of Stokes shift $(\Omega_0 - \Omega_2)$. The broken lines are theoretical plot of eq. (4). Ω_1 in the figure should be read as Ω_0. Taken from Ref. (4).
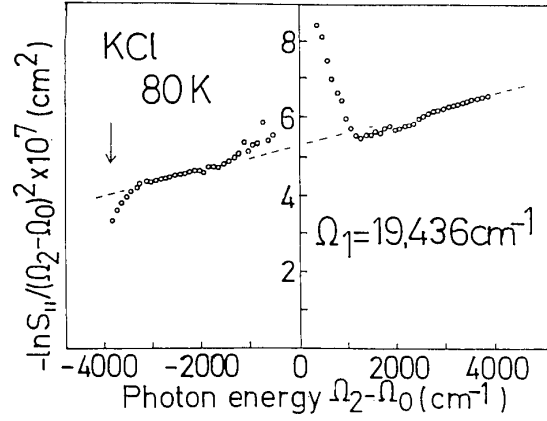
Fig. 5　The spectrum OL for F center in KCl at 80K versus photon energy of $(\Omega_2-\Omega_e)$. Ordinates are $[-\ln S/(\Omega_2 -\Omega_e)^2]$. Broken lines are theoretical plot from eq. (6). Ω_0 in the figure should be read as Ω_e. Taken from Ref. (3).

tail of the OL band. The shape function of the OL band, $S_P(\Omega_2)$, at the photon energy of Ω_2, is represented as following, adopting the Franck and Condon principle,

$$S_P (\Omega_2)\propto \int exp \{- We(Q_l)/kT\}\cdot$$
$$\delta\{We(Q_l)- W_g(Q_l)-\Omega_2\}dQ_l. \tag{5}$$

If assuming that the quadratic electron-phonon interaction terms in the APE of $We(Q_l)$ and $W_g(Q_l)$ are presented by introducing the different effective force constants of K_e and K_g in the OES and GS, the shape function of OL peaked at Ω_e is derived as following.

$$S_P(\Omega_2) \fallingdotseq exp\ [(-K_e/2c^2kT)(\Omega_2-\Omega_e)^2$$
$$\{1-(K_e-K_g)(\Omega_2-\Omega_e)/c^2\}], \tag{6}$$

where c is a quantity $(= K_g^2Q_e^2)$ related to a linear coupling constant, b, through Q_e $=(-b/K_e)$. A quantity $-\ln S_{//}/(\Omega_2-\Omega_e)^2$ is plotted in Fig. 5 with white circles as a function of $(\Omega_2-\Omega_e)$. The dotted lines are theoretical plots of eq. (6). Coincidence between experimental data and theoretical plot is quite nice except neighborhood of Ω_e. This incoincidence is due to the less invalid approximation to derive eq. (6). One more incoincidence is observed at the lower energy tail of OL band which is marked by arrow. This may reveal the enhancement of HL as was expected from the classical turning point. This surely verifies the validity of the damping oscillator model.

It is predicted from eq. (6) that the ordinates $-\ln S_{//}/(\Omega_2-\Omega_e)^2$ is independent of $(\Omega_2 -\Omega_e)$, in the case when $K_e = K_g$. Thus, the coincidence of dotted lines with data as shown in Fig .5 shows evidently that the inequality relation of $K_e\langle K_g$ does exist. It should be noticed that our result is quite contrary from so far accepted scheme of the APE in which $K_e = K_g$ was adopted[30]. Asami et al. pointed out that the latter APE scheme would be insuitable to explain their pressure effect on the OL band without introducing anharmonic potential term[31]. They suggested that the relation of $K_e\langle K_g$

would be a second best model.

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References

1) Y. Mori, R. Hattori, and H. Ohkura:J. Phys. Soc. Japan, **51**, (1982) 2713.

2) Y. Mori, R. Hattori, and H. Ohkura:Radiat. Eff. **72**, (1983) 283.

3) Y. Mori, H. Hanzawa, and H. Ohkura:J. Lumin. **38**, (1987) 159.

4) Y. Mori, and H. Ohkura:J. Phys. Chem. Solids **51**, (1990) 663.

5) Y. Kondo, A. Noto, S. Sato, M. Hirai, and A. Nakamura:J. Lumin. **38**, (1987) 164.

6) Y. Toyozawa, and M. Inoue:J. Phys. Soc. Japan **21** (1966) 1663.

7) F. S. Ham:Phys. Rev. **B 8** , (1973) 2926.

8) F. S. Ham and U. Grevsmühl:Phys. Rev. **B 8** , (1973) 2945.

9) Y. Kayanuma, and Y. Toyozawa:J. Phys. Soc. Japan **40**, (1976) 335.

10) Y. Kayanuma:J. Phys. Soc. Japan **40**, (1976) 363.

11) L. D. Bogan, and D. B. Fitchen:Phys. Rev. **B 1** , (1970) 4122.

12) H. Ohkura, K. Imanaka, O. Kamada, Y. Mori, and T. Iida:J. Phys. Soc. Japan **42**, (1976) 2137.

13) K. Imanaka, T. Iida, and H. Ohkura:J. Phys.Soc. Japan **43**, (1977) 519.

14) R. E. Hetrick, and W. D. Compton:Phys. Rev. **155** (1967) 649.

15) N. Akiyama, K. Asami, M. Ishiguro, and H. Ohkura:J. Phs. Soc. Japan **50** (1981) 3427.

16) G. Baldacchini, U. M. Grassano, and A. Tanga:Phys. Rev. **B16** (1977) 5570.

17) G. Baldacchini, U. M. Grassano, and A. Tanga:Phys. Rev. **B19** (1979) 1283.

18) H. Ohkura, K. Tara, N. Akiyama, K. Iwahana, and Y. Mori:J. Phys. Soc. Japan **51**, (1982) 3615.

19) H. Ohkura:Cryst. Latt. Def. amorph. Matter. **12**, (1985) 401.

20) N. Akiyama and H. Ohkura:Phys. Rev. **B40**, (1989) 3232.

21) K. Imanaka T. Iida, and H. Ohkura:J. Phys. Soc. Japan **44**, (1978) 1632.

22) K. Iwahana, T. Iida, and H. Ohkura:J. Phys. Soc. Japan **47**, (1979) 599

23) C. H. Henry and C. P. Slichter:*Physics of Color Centers*, ed. by W. B. Fowler (Acad. Press, N. Y., 1968) Chapter 6.

24) J. C. Buchenauer, D. B. Fitchen, and J. B. Page:*Light Scattering of Solids*, ed. by G. B. Wright (Springer Verlag, Berlin, 1969) p. 521.

25) D. S. Pan, and F. Lüty:*Light Scattering in Solids*, ed. by M. Balkanskii, R. C. Leite, and S. P. S. Port (Flammarion, Paris, 1975) p. 513.

26) M. A. Aegerter, and F. Lüty:Phys. Stat. Sol. (b) **43**, (1971) 245.

27) Y. Kayanuma, Y. Mori, and H. Ohkura:J. Lumin. **38**, (1987) 137.

28) Y. Kayanuma:J. Phys. Japan **57**, (1988) 292.

29) W. Gebhardt, and H. Kühnert:Phys. Stat. Sol. **14**, (1966) 157.

30) R. H. Bartram:J. Phys. Chem. Solids **51**, (1990) 641.

31) K. Asami, T. Naka, and M. Ishiguro:Phys. Rev. **B34**, (1986) 5658.