Working Principles of the Optical Detection Methods of ESR, ENDOR, and ZF-ENDOR for the Relaxed Excited State of the *F* Centers

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Abstract

Qualitaitve explanation of working principles of the optical detection (OD) methods of ESR, ENDOR and ZF-ENDOR for the study of the relaxed excited state (RES) of *F* centers are presented. The ZF-ODENDOR method is a sort of the ENDOR technique measured without sending any resonant elelctromagnetic waves. It had been developed in Jaccard's school. They have observed a few series of signals due to the super hyperfine (shf) interaction in the ground state (GS), when the *F* centers in KCl are excited optically. We propose a working principle of ZF-ODENDOR , and predict that shf signals of the RES can be measured. After improving the ZF-ODENDOR method, Akiyama and Ohkura in the Okayama University of Science have observed the shf constants in the RES, with which they have determined the envelope function of the RES of the *F* centers in KCl. This verifies the vibronic scheme of the RES proposed by us previouly.

§1. Introduction

The investigation of the optically excited states (OES) in solids is one of the most attractive research fields at present not only for its academic interest but also because of industrial interest in the development of optoelectronics. In particular, the study of the *F* centers in alkali halides can provide useful knowledge about the OES particularly of defects with deep electronic state in condensed matter. The information obtained can be extended to the research of the OES in bulk solids which naturally include defects as a limiting case.

The *F* center is one of the most typical and simplest defects in solids. It consists of an electron trapped by an anion vacancy in alkali halides with a simple cubic crystal structure[1]. During this centural period since the discovery of the *F* center, the study of the *F* center has played essentially the same role in the solid state physics as that hydrogen atom has achieved to establish the quantum mechanics. One of the most specific difference of the *F* center from the hydrogen atom lies on a fact that it is sited at the crystalline lattice. Thus, it is governed more or less by the interaction of the phonon fields. The study of electronic processes in the F centers would be impossible if excluding the electron-phonon interaction.

Almost all of *the electronic structure* of the ground state (GS) of paramagnetic color centers including the F center has been determined through the magnetic resonance (MR) studies[2]. In 1953, the model and structure of the GS of the F centers described above was firstly confirmed through the study of electron spin resonance (ESR) by Kip et al.[3]. The detailed structure of the GS of the F centers was determined through the electron nuclear double resonance (ENDOR) technique which was invented by Feher in 1958[4]. As these measurements have been carried out for the stationary state of the GS, they are classified as direct and stationary ESR and ENDOR methods. However, the MR research for the relaxed excited state (RES) of the F centers, which is the thermalized OES and corresponds to the initial state for the F center luminescence, is much difficult work if one could use the stationary ESR or ENDOR apparatus which have been used for the measurements of the GS. This depends on a principle that the MR intensity is proportional to the spin density, or exactly speaking, the spin polarization as will be discussed in §3. During the optical excitation, the stationary spin density in the RES is reduced from that of the GS by a factor of the radiative lifetime of the RES being short of less than nearly μ second[5]. This is too small to be detected. In order to solve this difficulty, three sorts of indirect methods have been proposed, and successfully developed[6]. As these methods are based on the optical detection (OD) of MR of the RES, they are called ODMR. Particularly, the OD method for ESR is called ODESR and that for ENDOR is ODENDOR. In 1978, a new ODENDOR method was developed at Jaccard's school in the University of Neuchâtel. They measured the ENDOR signals at the third and fourth shells in the GS surrounding the anion vacancy without sending any rf or microwave for the resonance[7]. Thus, it is called ZF-ODENDOR.

Recently, Akiyama et al. in the Okayama University of Science have improved the ZF-ODENDOR method[8], and postulated that the ENDOR signals for the RES are measurable[9]. Akiyama and Ohkura have determined the normalized envelope wavefunction of the RES that is composed mostly of the $2s$-like admixed by small amount of $2p$-like through the electron-lattice interaction[10]. This electronic structure is coincident with that proposed by Bogan and Fitchen[11] which is the two-level approximation of the vibronic model of the RES derived by many authors including us[12~14]. This article is particularly devoted to introduce the working principles of the experimental methods of ODESR, ODENDOR, and ZF-ODENDOR of the RES tested so far.

The present work is organized as follows. In §2, spin Hamiltonian of the spin system of an unpaired electron in the F center is presented. Theoretical forms of the ODENDOR and ZF-ODEDOR spectra are presented, In §3, experimental methods and their working principles of ODESR and ODENDOR, which had been done for the GS of F centers previously, are reviwed briefly. In §4, the ZF-ODENDOR results for the GS done at Jaccard's school are presented. In §5, a novel working principle of the ZF-

ODENDOR method is proposed qualitatively. In §6, recent works on the ZF-ODENDOR of the RES of the *F* centers in KCl are briefly described. Results are summarized in §7.

§2. Spin Hamiltonian of the *F* centers

Let us introduce the theoretical form of the Zeeman-split energy levels of the unpaired electron in the *F* center which is coupled with surrounding nuclei with the super-hyperfine (*shf*) interaction[2]. When a static magnetic field $\boldsymbol{B}_0$ is applid along the z-direction, the spin Hamiltonian is written as follows[6,15],

$$\boldsymbol{H} = g_e\beta_e\boldsymbol{B}_0\boldsymbol{S} + \Sigma_\ell(\boldsymbol{S}\cdot\mathbf{A}_\ell\cdot\boldsymbol{I}_\ell - g_{n\ell}\beta_n\boldsymbol{B}_0\boldsymbol{I}_\ell), \tag{1}$$

where the sum is taken over all nuclei labeled ℓ surrounding an anion vacancy, here, g_e is the electron g-factor, β_e is the Bohr magneton, $g_{n\ell}$ the nuclear *g*-factor at the ℓ site nucleus, β_n the nuclear magneton, $\boldsymbol{S}$ the electron spin operator and $\boldsymbol{I}_\ell$ the nuclear spin operator at $\boldsymbol{r}_\ell$, respectively. The quadrupole interaction is neglected for convenience. The shf tensor $\mathbf{A}_\ell$ is usually decomposed into an isotropic $a_\ell\mathbf{1}$ and an anisotropic part $\mathbf{B}_\ell$, according to

$$\mathbf{A}_\ell = (a_\ell\mathbf{1} + \mathbf{B}_\ell), \tag{2}$$

where a_ℓ is the isotropic shf constant (Fermi contact term), and $\mathbf{1}$ is a unit diagaonal tensor[2]. When we choose a principal axis system of the shf tensor, $\mathbf{B}_\ell$ can be simplified as following with reference to x_ℓ, y_ℓ, z_ℓ axes, which are taken to be coincident with the crystalline axes,

$$b_\ell = (1/2)B_{\ell,\,zz} \tag{3a}$$

and

$$b_\ell' = (1/2)(B_{\ell,\,xx} - B_{\ell,\,yy}), \tag{3b}$$

where b_ℓ is called the anisotropic shf tensor and b'_ℓ is the deviation along the z direction. We assume that the largest interaction is along the z direction.

In §5, we show that non-diagonal component of spin Hamiltonian, $\mathfrak{H}_{\mathrm{fl}}$, neglected here has a <u>*time-dependent form*</u> of $(\boldsymbol{I}_x\mathbf{A}_\ell\boldsymbol{S}_x + \boldsymbol{I}_y\mathbf{A}_\ell\boldsymbol{S}_y)$. This may play essential role for experimental performance of ZF-ODENDOR, that is one of main objects to be discussed.

Gourary and Adrian derived the a and b values at the ℓ-th nucleus as follows[15].

$$a_\ell = (2/3)\mu_0 g_e\beta_e g_{n\ell}\beta_n A_\ell|\Psi_0(r_\ell)|^2 \tag{4}$$

$$b_\ell = \mu_0 g_e\beta_e g_{n\ell}\beta_n B_\ell|\partial\Psi_0(r)/\partial r|^2_{r=r_\ell}, \tag{5}$$

where μ_0 is ($4\pi \times 10^{-9}$ *V-sec/A-cm*), $\Psi_0(r_\ell)$ is a normalized envelope wavefunction measured at the nucleur site of r_ℓ. The quantity A_ℓ in eq. (4) is a proportionality constant introduced by Gourary and Adrian to account for the oscillating character of $\Psi_0(r_\ell)$ due to the overlapping with ion core functions at the site r_ℓ because of the Pauli principle. A_ℓ is called amplification factor.

The b_ℓ-value in eq. (5) is the anisotropic shf interaction constant at the ℓ-th nucleus which represents the classical dipole-dipole interaction between the unpaired F electron and the surrounding nuclei. A proportionality constant B_ℓ in eq.(5) is introduced as the similar manner as to introduce A_ℓ[15]. With these considerations, the eigenvalue of eq. (1) is derived as,

$$E = g_e\beta_e B_0 m_s - g_{n\ell}\beta_n B_0 m_{\ell I} + m_s m_{\ell I} W_{\mathrm{shf}}, \tag{6}$$

with

$$W_{\mathrm{shf}} = a_\ell + b_\ell(\cos^2\theta_\ell - 1) + b_\ell' \sin^2\theta_\ell \cdot \cos 2\delta_\ell, \tag{7}$$

where m_s and $m_{\ell I}$ are the spin quantum numbers of the z-components of spin operators, $\boldsymbol{S}$ and $\boldsymbol{I}_\ell$, and θ_ℓ and δ_ℓ are polar angles of B_0 in the principal shf axis system[6,15].

The usual ENDOR transition occurs with selection rule as shown $\Delta m_s = 0$ and $\Delta m_{\ell I} = \pm 1$. Thus, it is derived as

$$\nu_{\mathrm{ENDOR}} = |(1/h)|ms|\, W_{\mathrm{shf}} \mp \nu_n| \tag{8}$$

with

$$\nu_n = (1/h) g_{n\ell}\beta_n B_0, \tag{9}$$

which is the Larmor frequency of a free nucleus in the magnetic field B_0.

Mezger and Jaccard suggested that ZF-ODENDOR occurs at a specific magnetic field B_{zf}, when $\nu_{\mathrm{ENDOR}} = 0$[16]. It is derived from eq. (8) as

$$B_{\mathrm{zf}} = (1/2)\, W_{\mathrm{shf}}/g_{n\ell}\beta_n. \tag{10}$$

for $m_s = (1/2)$. They pointed out that B_{zf} is independent of isotope effect by nuclei, since the numerator in eq. (10) is included in the denominator as shown in eqs. (4) and (5).

Equation (3) implies that, if the values of A_ℓ were known, the shape of the $\Psi_0(\boldsymbol{r})$ is determined as a function of distance $\boldsymbol{r}$ from the center of anion vacancy. However, it is difficult to calculate theoretically the A_ℓ values for surrounding nuclei[18,20]. In the previous works[2,17,18], it has been commonly assumed that the A_ℓ values for each cation are all the same and those for each anion are also the same, although they are not the same each other. With this assumption, the $\Psi_0(r)$ has been determined not only for the GS but RES[2,16~18]. On the other hand, Fowler and Kunz claimed the validity of this assumption[19].

On this occasion, we are faced to compete the validity of $\Psi_0(r)$, which has been proposed by us after consistent explanation of the experimental data obtained[9,10,14], with another $\Psi_0(r)$, which has been proposed from the analysis of the ODENDOR[17,21]. This is one of the reasons why we carried out the present ZF-ODENDOR measurement. However, for the calculation of the $\Psi_0(r)$ from a_ℓ obtained from the ZF-ODENDOR method, we need to choose the A_ℓ values. Although Fowler and Kunz's claim was not resolved, we adopt the same assumption as the previous works. This is because, for the competetive discussion, it might be better to stand on the same background.

§3. ODMR studies of the RES of the *F* centers.

We discuss the working principles of three different OD methods for the indirect MR method as introduced in §1. We separate them into two cases depending on the (low and high) concentrations of *F* centers included. When the *F* centers in densely colored specimens are optically excited, a *temporarily paired F centers* is formed between the RES and GS. We discuss some detail of this pair in §3. 2.

(3.1) Isolated *F* centers: low *F* concentration.

Two sorts of the ODMR methods have been develpoed on the basis of the specific magneto-optical processes of the isolated *F* centers in the specimens with low *F* concentrations. {less than about $3\times10^{16}\,(cm)^{-3}$}. The first method is based on **magnetic circular dichroism** (MCD) in the optical absorption of the *F* centers[21]. MCD is divided into two components of dia-and para-magnetism[25]. Its paramagnetic component is proportional to a spin polarization P_s in the Zeeman-split system in the GS[22]. It is defined as

$$P_s = (n_- - n_+)/(n_+ + n_-), \tag{11}$$

where n_+ and n_- are the spin populations in the Zeeman levels corresponding to $m_s = \pm\,(1/2)$ in the GS. On the other hand, the spin Zeeman polarization in the RES, P_s^*, is similarly defined as,

$$P_s^* = (n_-^* - n_+^*)/(n_+^* + n_-^*), \tag{12}$$

where $n_\pm^*$ are the spin populations in the Zeeman levels in the RES. During the optical pumping cycle of the *F* center at liquid He temperatures under the saturated optical pumping condition, in which the pumping rate of the *F* center exceeds the spin lattice relaxation rate[23,24,26]. This causes the nonequilibrium P_s and P_s^*, whose forms are derived from the steady-state solution of the rate equations. The result shows that the P_s is related to the P_s^*.

Therefore, when the ESR transition between electron spin Zeeman levels either in the GS or RES is induced by sending resonant microwave oscillating transversely to the z-direction, the spin polarization can be reduced. Thus, the intensity of MCD in the nonequilibrium states is reduced at the resonant B_0, by which we can observe the ESR of the both GS and RES. The work was firstly tried by Baldacchini and Mollenauer[21]. Mollenauer and Pan derived the detailed analysis for dynamical processes[23,24] Mollenauer and Baldacchini extended this method for the detection of ODENDOR of the RES[17].

Thereafter, Winnacker's school in the Univerity of Heidelberg carried out precise measurement of ODESR of the RES using MCD[18]. They have shown ODESR data for the RES of KCl, KBr, and KI[18].

The second type of the ODESR method was developed by us in the Osaka City University[25,26]. Before committed into ODESR, we have interested in interpreting the experimental facts reported by Baldacchini *et al.*[27]. They had shown that the magnetic field dependences of the **magnetic circular polarization** (MCP) of F centers luminescence are dependent on the polarization of the excitation laser light, either with linear or circular polarization. As they had left their observation unexplored, we tried to clarify them by recognizing that MCP is composed of the dia-and para-magnetic components[25,26], and derived that the latter component is proportional to the P_s* defined in eq. (12) under the saturated pumping conditions. Here, we used Winnacker *et al.*'s idea that the spin mixing parameters on the optical absorption depends on the circular polarization of resonant light[28,29]. Let us remark that the Winnacker *et al.*'s scheme has been established quantum mechanically by Muramatsu *et al.*[30]. A little later, Baldacchini *et al.* independently derived the same conclusion as ours[31].

Then, we noticed that the P_s* can be controlled by the ESR transition in the Zeeman levels that leads to vary the spin polarization either in the GS or in the RES. This is the second working principle of the ODESR methods for the GS or RES.[24~26]. In fact, we succeeded in observing ODESR by adopting the Faraday configuration, in which the excitation light propagates through a specimen along the same direction as B_0. No ODENDOR method using this MCP-controlled ODESR has been tried yet.

(3.2) Temporary pair of the *F* centers formed under optical excitaion.

The third kind of the ODMR method has been established for the specimens colored moderately or rather densely. In 1970's, Jaccard's school in the University of Neuchâtel studied systematically the spin system in such specimens[32~34]. Suppose when the isolated F center is optically excited, its orbital is so widely spread during the lattice relaxation until finally thermalized into a metastsble state, that is the RES[35], whose radius is estimated to be 4 nm[7,9,35]. Notice that this is almost equivalent to a mean distance of a pair of F centers in the GS in the case when 10^{18} $(cm)^{-3}$ of F centers were uniformly distributed in a crystal. Thus, when a colored KCl with $\sim 10^{17}$ F centers $(cm)^{-3}$ is optically excited, one may expect that a certain amount of the F centers in the RES can be paired temporarily with a nearby-lying another F center in the GS. We call this pair a **temporary pair of *F* centers**. Occasionally, in the temporary pair, the RES electron can nonradiatively form an F' center via tunneling leaving a vacancy behind transiently. Thereafter, this transient state is subsequently de-excited to return into two dissociated F centers nonradiatively. As a whole, the formation of temporary pairing causes a possibility to undergo new channel of *non-radiative de-excitaiton process of the RES* in the optical pumping cycle of the F centers. Jaccard *et al.* have proposed that two types of temporary pairs of the F centers may exist in the optically excited alkali halides colored densely: One is a close pair (CP) and another is a distant pair (DP) depending on the mean distances of pairing centers. {about 2~4 nm for the CP, and 8 nm for the DP}. They are distinguished experimentally. Namely, in the ESR spectrum for the CP, specific exchange effect appears, but not for the DP[36,37]. One more characteristic difference is in the signs of the ODESR dips found in the magnetic field depencence of the *F* center luminescence; negative sign for the DC, positive for the CP. In the present work, we mostly concentrate to study the *F* centers in a moderately colored specimen in which the DP are predominantly contained. The present work is limited to discuss the optical processes related to the DP, unless otherwise stated.

The evidence of the temporary *F* centers pair was firstly confirmed by a qualitative explanation of an experimental fact that the quantum efficiency of the *F* luminescence, η_F, is reduced when the the *F* concentrations are increased beyond $10^{17}\,(cm)^{-3}$: This fact is called **concentration quenching of η_F**[38]. The reduction of η_F can be explained basically in terms of the increase of non-radiative process that occurs with increase of *F* concentrations.

Later, Porret and Lüty showed that the reduced η_F is recovered with increase of magnetic field (B_0) applied[39]. This effect is called the Porret-Lüty effect. This can be explained in terms of the change in the spin symmetry in the temporary DP *F* centers reflecting the Pauli principle. With increase of B_0, a certain fraction of spin triplet component in the temporary DP *F* centers formed during the optical excitation may be naturally increased as an expense of the spin singlet state. The increse of spin triplet in the temporary DP causes the decrease of nonradiative process via tunneling because of the Pauli principle, thus resulted in the recovery of η_F.

(3.3) Working principle of ODESR and ODENDOR based on the Porret-Lüty effect

One may suspect that the Porret-Lüty effect can be controlled artificially by ESR transition caused by resonant microwave to the Zeeman levels either in the GS or RES at a finite resonant magnetic field. This is a working principle for the third type of ODMR method. Namely, artificial inversion of the fraction of triplet spin state into the singlet state in the the temporary DP will give ODESR of the GS and RES. In fact,we proposed that ODESR can be observed in the magnetic field depndence of η_F if the specimen is sited in a resonant cavity with a finite microwave frequency.

Before the discovery of the Porret and Lüty effect, Ruedin and Porret observed ODESR of the RES of KCl in 1969[40]. However, because of very close g_e-values for the GS and RES, the separation of both ESR traces was seemingly inclear at the X-band microwave. After stimulated by the discovery of the Porret and Lüty effect, we tried to measure ODMR of the RES of F_A centers in KCl[41]. Murayama *et al.* observed ODMR of *F* centers RES in KCl in which they found the trace of exchange coupled *F* center pairs[42]. Baranov *et al.*[43] and Romanov *et al.*[44] have measured the ODENDOR spectra of the RES for NaCl, KF, KCl, KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr, and CsI. Particularly, in Ref. 44, they measured the RES in ^{41}KCl and proposed that the RES consists of compact 2*s*-like wavefunction.

Finally, we emphasize that the parameters to describe several important quantities of magnetic natures of the RES, which have been determined from the ODMR study of the RES for the *F* centers, are found to be almost the same amounts. This fact reveals the validity and preciseness of the ODMR methods, even if they were obtained by indirect methods.

§4. The ZF-ODENDOR studies of the GS

In 1978, Jaccrd and Ecabert have reported that a certain numbers of dips in η_F with a faint intensity can be observed at a finite magnetic field, B_{zf}, in the precisely measured magnetic field dependence of η_F without sending resonant rf or microwaves. They have noticed that dips appear in the decreasing direction of η_F. (Note that the intensity of F luminescence is proportional to η_F). Furhtermore, when rf wave of frequency ν was sent to the specimen, Ecabert has observed that a series of dips at $B_0(\nu)$ satisfying eqs. (8) and (9) appear newly in the similar way as ENDOR. When ν is varied, $B_0(\nu)$ is shifted so as to satisfy eqs. (8) and (9), while the dip at B_{zf} remains unchanged[45]. Note that no microwave was sent. He has confirmed that these series of $B_0(\nu)$ are reduced to B_{zf} at the zero frequency (ZF) where $\nu_{ENDOR} = 0$. They have proposed that W_{shf} for the GS in the temporary DP of the F centers can be solely determined[16]. Howerer, no mentioning have been made for the RES.

They have proposed the working principle of the ZF-ODENDOR method[45]. According to the Porret and Lüty effect, the decreasing tendency of η_F dips observed at B_{zf} is related to the occurrence of nonradiative relaxation processes. By considering the spin symmetry that may occur in the temporary DP F centers, they have proposed two mechanisms which may cause nonradiative processes at the ZF-ODENDOR conditions. One is that a fraction of spin triplet state in the DP is transferred to a spin singlet state by a perturbation due to B_0. The second is the idea that the formation of the temporary spin triplet by tunneling is prohibited because of the Pauli principle. However, it is hard to decide which processes might be predominant. In addition to these processes, they have intuitively proposed that, if smoothly varying B_0, the crossing of one of the *shf* levels with the nuclear Zeeman levels may occur at B_{zf} in eq. (10), which undergoes to invert the spin triplet to singlet, so that reducing η_F.

As the signal intensity is so faint that they could hardly identify except the ZF-ODENDOR signals due to Cl in the forth shells and K in the third shells in the GS coupled with shf interaction[45]. Moreover, they observed several series of finite ZF-ODENDOR signals in the higher magnetic field range than 0.15 T. They attributed them to unknown paramagnetic centers[16]. We convince that these η_F dips observed may originate from the shf signals from the RES, because the shf signals for the GS would never appear in the higher magnetic field range than 0.15 T. In the next section, we show the reason why these are realted to ZF-ODENDOR of the RES.

§5. Our working principle of ZF-ODENDOR

Here, independent of Mezger and Jaccard's proposed model introduced in §4, we propose a novel working principle in a qualitative fashion. When the static magnetic field, B_0, is applied along z-direction, the electron spin polarization $\langle S_z \rangle B_0$ is produced along the z direction according to the first term in eq. (1). The second term in eq. (1)

can be equivalently replaced by a fictitious nuclear Zeeman interaction $\mathfrak{H}_{n\ell}$ for the ℓ-th nucleus seen by a fictitious magentic field $\boldsymbol{H}_{n\ell}$ that is produced by the $\langle \boldsymbol{S}_x \rangle$ being the x-component of $\boldsymbol{S}$. Both quantities are presented as follows

$$\mathfrak{H}_{n\ell} = g_{n\ell}\beta_n \boldsymbol{H}_{n\ell}\boldsymbol{I}_\ell, \tag{13}$$

and

$$\boldsymbol{H}_{n\ell} = A_\ell \langle \boldsymbol{S}_x \rangle / g_{n\ell}\beta_n. \tag{14}$$

Here, even if $\langle \boldsymbol{S}_x \rangle = 0$, we remind that the root mean square value of $\boldsymbol{S}_x$ has finite value of $\langle \boldsymbol{S}_x{}^2 \rangle = 1/4$, which may play an important role *in the second order perturbation scheme*. Now, from eq. (14), we may asssume that the ℓ-th nucleus could rotate coherently around the x-cmoponent of $\boldsymbol{H}_{n\ell}$, $\boldsymbol{H}_{n\ell}(x)$, with a Larmor frequency of $\omega_n = A_\ell \sqrt{\langle \boldsymbol{S}_x{}^2 \rangle}/\mathrm{h}$. We may suspect that this is seemingly the same experimental situation as that of the nuclear magnetic resonance for the ℓ-th nucleus under application of B_0 along the z-direction where the oscillating magnetic field of the intensity $\boldsymbol{H}_{n\ell}(x)$ with coherent angular frequency ω_n is applied transversely.

Thus, if one stands on a rotary coordinate rotating with the angular frequency ω_n along the z-direction, the nucleus will precess around a rotary effective magnetic field of B_{eff}, which is shown as,

$$B_{\mathrm{eff}} = B_0 - \omega_n / \gamma_{n\ell}, \tag{15}$$

where $\gamma_{n\ell} \equiv (g_{n\ell}\beta_n/h)$ is a gyromagnetic ratio for the ℓ-th nucleus. Therefore, when B_0 is swept over **so slowly as to satisfy the adiabatic rapid passage condition**, the nuclear polarization of the shf coupled with ℓ-th nucleus, precessing around the direction of B_{eff} beforehand, will tend to fall down on the x-y plane at the resonant condition where $B_{\mathrm{eff}} = 0$ in eq. (15)[46]. This resonant process might be theoretically formulated as a time-dependent perturbation effect caused by the off-diagonal Hamiltonian, $\mathfrak{H}_{\mathrm{fl}}$, which has a form of $(\boldsymbol{I}_x A_\ell \boldsymbol{S}_x)$as Shown in §2 . Thus, $\langle \boldsymbol{S}_x \rangle$ in eq. (14) can be replaced by $\sqrt{\langle \mathbf{S}_x{}^2 \rangle} = 1/2$ in the second order perturbation. Hence, B_0, which is deduced from eqs. (14) and (15) is found to be equal to B_{zf} in eq. (10).

Thus-fallen nuclear spin would produce (fanning out) fluctuating magnetic fields in the x-y plane that operate back to the electron spin polarization to invert its sign as in the similar way as in pulse NMR. Namely, the nuclear fluctuating fields will give rise to counter reaction to the electron spin polarization system to cause spin flipping dynamically. In fact, the spin inversion occurs in the case when the Fourier transform (a power spectrum) of the correlation function of the fluctuating magnetic fields could have a sizable component at the electron spin Zeeman frequency[46].

Let us consider the spin symmetry in the temporary DP. As described in §3.2, the inversion of the electron spin state from a triplet into a spin singlet causes a nonradiative process,[39] which results in decrement of η_{F} in its magnetic field dependence characteristics. Inversely speaking, a small decrement dip of η_{F} observed at B_{zf} reveals the inversien of spin symmetry. So that, using eq. (10) for B_{zf}, one can obtain the *shf*

-ENDOR spectrum. As the spin inverstion can occur either in the GS or the RES, the a_ℓ and b_ℓ spectra for both states can be determined, respectively. This is the *working principle of ZF-ODENDOR* which is proposed here.

Our proposal can be approved qualitatively from the following two experimental facts. In the ZF-ODENDOR measurement by adopting magnetic field modulation method, we found that the intensity of the η_F dip is decreased vanishingly with increasing the modulation frequency, ω_n, of superimposed ac magnetic field on slowly varying B_0[42]. Finally, the dip intensity is decreased to its one-half at the finite ω_n, which corresponds to the inverse of the nuclear spin lattice relaxation time T_1. This is a convincible evidence that the rapid passage condition is satisified.

The last evidence is an experimental fact observed by Ecabert[45]. As has been introduced in § 4, when the resonant rf field is applied in the ZF-ODENDOR measurement, both the ENDOR and the ZF-ODENDOR spectra are observed to be co-existent, even if without sending microwave for the excitation of the electron spin system. The former spectrum depends on ν_n to satisfy the usual ODENDOR condition in eq. (8) through eq. (9), while the latter sapectrum is independnet of ν_n to follow eq. (10). This is a convincible evidence that the rotary coordinate scheme as shown in eq. (15) can be applicable for ZF-ODENDOR.

§6. Brief results by the ZF-ODENDOR study of the RES

In 1989, Akiyama *et al.* (including the author) improved the SN ratio of Metzger and Jaccard' ZF-ODENDOR method by paying special experimental care[8]. They could reproduce the same ZF-ODENDOR signal as in Ref. 16, and also could observe a new shf signals due to the K nuclei at the V-th shell in the GS. They have found that these shf signals show characteristic dependence on the angles between the crystalline axis and the B_0 applied: This is worth to report. From the curve-fitting analysis of the angular dependence using theoretical forms derived fundamentally from eq. (7), the shf interaction constants of a_ℓ and b_ℓ values in eqs. (4) and (5) are determined. It is confirmed that these values determined for the GS are all the same as those determined by the stationary ENDOR for the GS previously[2].

Racently, we have also observed the shf signals in the higher magnetic field range than that for the GS mentioned above, and identified them to be the shf signals from the RES. These were the same signals as were observed but left unidentified in Ref. 16. Again, from the curve-fitting analysis of their angular dependence, the a_ℓ and b_ℓ values for the RES are determined over the 32 shells[9,10]. With these a_ℓ values, the normalizeed envelope wavefunction of the RES has been calculated, by adopting several assumption including the choice of the A_ℓ values discussed in §3. Thus calculated envelope wavefunction of the lowest RES consists of the $2s$-like wavefunction admixed by 13% of $2p$-like wavefunction. This form is quite the same as that derived from the two-level approximation of the vibronic scheme of the RES that had been determined previously from consistent analysis of the Stark effect and the temperature dependence of the F luminescence[12~14]. Note that this model is basically coincident with Bogan and Fitchen model of the RES[11]. On this occasion, we emphasize that this conclusion leads to cease the conflict between the previous work by Mollenauer and Baldacchini [17,21] and ours. The former group has insisted that the RES consists of widely spread $2p$ wavefunction from their ODENDOR analysis[9,10]. In a recent analysis, we have shown that their ODENDOR spectrum for KBr and KI can be reproduced well with our results of ZF-ODENDOR[47]. The result will be published.

§7. Summary

Three sorts of working principles for ODESR and ODENDOR of the RES of the F centers, which were developed previously, have been compiled. In addition to these, the working principle of ZF-ODENDOR, which has been intuitively proposed by Metzger and Jaccard solely for the ENDOR study of the GS, is newly proposed in the present work from a different viewpoint and postulated that the method can be extended for studying the RES. Let us clarify our idea qualitatively in the following. We point out that a triplet spin in the temporarily formed distant pair (DP) of F centers (namely, the RES and a neighboring GS) can be inverted into a singlet spin when the nuclear system coupled with shf interaction with electron system is second orderly perturbed by the adiabatic rapid passage of static magnetic field applied. Such an inversion of spin symmetry may occur both in the shf coupled GS and RES. In the optical sense, such a total spin inversion in the temporary DP may convert the radiative relaxation process into the nonradiative relaxation in the optical cycle of the F center under the adiabatic rapid passage condition of magnetic field applied. This causes the decrease in η_F. Thus, the η_F dips observed at a specific magnetic field, B_{zf}, in the magnetic field dependence of the F luminescence, are related to the shf-coupled nuclear levels either in the GS or the RES, through eq. (10). From the a_ℓ and b_ℓ values determined for the RES, we have figured out the normalized envelope wavefunction of the RES, which is composed of $2s$-like admixed by 13% of $2p$-like via the electron phonon interaction. The fact verifies the validity of the vibronic scheme which has been established so far to explain all experimantal facts related to the RES consistently[11~14].

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