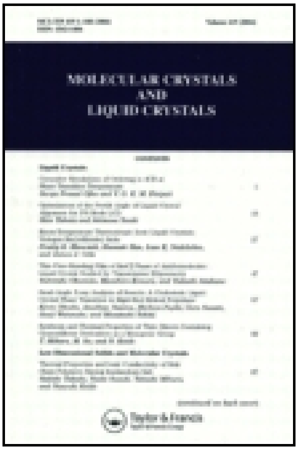

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spin Characterization of Lanthanoid Ion $Eu^{2\pm}$ ($^8S_{7/2}$) in a CaF_2 Single Crystal by Electron Spin Transient Nutation Spectroscopy

Kazunobu Sato [a] , Hideto Matsuoka [a] , Daisuke Shiomi [b] , Takeji Takui [a] & Koichi Itoh [b]

[a] Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

[b] Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558-8585, Japan

Version of record first published: 24 Sep 2006

To cite this article: Kazunobu Sato, Hideto Matsuoka, Daisuke Shiomi, Takeji Takui & Koichi Itoh (1999): Spin Characterization of Lanthanoid Ion $Eu^{2\pm}$ ($^8S_{7/2}$) in a CaF_2 Single Crystal by Electron Spin Transient Nutation Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 333-342

To link to this article: http://dx.doi.org/10.1080/10587259908028877

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 333-342
Reprints available directly from the publisher
Photocopying permitted by license only

Spin Characterization of Lanthanoid Ion Eu^{2+} ($^8S_{7/2}$) in a CaF_2 Single Crystal by Electron Spin Transient Nutation Spectroscopy

KAZUNOBU SATO[a], HIDETO MATSUOKA[a], DAISUKE SHIOMI[b], TAKEJI TAKUI[a] and KOICHI ITOH[b]

[a]*Department of Chemistry and and* [b]*Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558–8585, JAPAN*

One of lanthanoid ions, Eu^{2+} ($^8S_{7/2}$), doped in a CaF_2 single crystal with cubic symmetry has been studied by an Electron Spin Transient Nutation (ESTN) method of pulsed ESR spectroscopy. In a two-dimensional ESTN spectrum of the Eu^{2+} ion, the nutation frequencies indicated the dependence of hyperfine ESR transitions as well as of spin quantum number S and M_S manifolds. It is demonstrated that the 2D-ESTN method discriminates the hyperfine allowed ESR transitions from the hyperfine forbidden ones. Such discrimination of the ESR transitions enables us to make facile assignments of complicated ESR spectra. The nutation frequencies observed for the hyperfine allowed / forbidden transitions were quantitatively understood with the help of reduced rotation matrix elements.

Keywords: transient spin nutation; pulsed ESR; single crystal ESR; lanthanoid ion; hyperfine forbidden transitions

INTRODUCTION

The recent advances in the field of molecular magnetics and spin chemistry have provided a variety of organic high-spin systems from high-spin molecules to spin clusters and extremely large high-spin polymers. Conventional ESR spectroscopy is very fruitful in studying physical properties of magnetic materials and has been applied to molecular magnetic materials in order to characterize their electronic states. With increasing effective spin quantum number S of molecular magnetic systems the conventional ESR method manifests its inherent disadvantages in resolving and discriminating ESR signals due to high-spin systems from those due to other spin systems such as a doublet impurity and in determining the effective spin quantum numbers for the complicated mixture composed of various spin systems. In order to overcome the difficulties we have developed an electron spin transient nutation (ESTN) method based on a pulsed ESR technique.[1-5] The ESTN method is based on electron spin resonance to measure the spin Hamiltonian in terms of the rotating frame. We have applied the field-swept two-dimensional ESTN (2D-ESTN) method to ordered or disordered high-spin systems, showing that the 2D-ESTN method discriminates ESR transitions arising from different spins in mixed high-spin systems, and unequivocally identifies the effective spin quantum numbers of high-spin species in the systems.

In this work, we have applied the 2D-ESTN method to one of lanthanoid ions, Eu^{2+} ($^8S_{7/2}$), doped in a CaF_2 single crystal with cubic symmetry. Electronic state of the Eu^{2+} ion in the CaF_2 single crystal has been studied and characterized well in 1960's by several groups.[6-8] Importance of higher-order terms (S^4 and S^6) in the spin-Hamiltonian is realized for understanding conventional ESR spectra of the Eu^{2+} ion. The ESR spectra of the Eu^{2+} ion indicate very complicated hyperfine structures, in which hyperfine forbidden transitions ($\Delta M_S = \pm 1$ and $\Delta M_I \neq 0$) are observed in addition to hyperfine allowed transitions ($\Delta M_S = \pm 1$ and $\Delta M_I = 0$). This paper focuses on the ESTN phenomena of the hyperfine ESR transitions in the high-spin states of the Eu^{2+} ion with nuclear spin ($I = 5/2$). It is demonstrated that the 2D-ESTN method is a powerful tool for discriminating between the hyperfine allowed and forbidden transitions in complicated fine-structure ESR spectra.

THEORY OF TRANSIENT NUTATION

Phenomenon of the electron spin transient nutation is considered using the time-dependent Schrödinger equation in a rotating frame. In the rotating frame, the Schrödinger equation is described as

$$i\hbar\frac{\partial}{\partial t}\Psi(t)=\mathscr{H}^{r}(t)\Psi(t) \qquad (1)$$

where $\mathscr{H}^{r}(t)$ is a rotating-frame Hamiltonian. The rotating-frame Hamiltonian is constructed by transforming a laboratory-frame Hamiltonian, $\mathscr{H}+\mathscr{H}_{1}(t)$, to the rotating frame that rotates about a z axis with an applied microwave frequency ω_{MW}. Here $\mathscr{H}$ and $\mathscr{H}_{1}(t)$ stand for the spin Hamiltonian which is given in Eq.(6) and an interaction Hamiltonian due to the irradiated microwave field, respectively. Considering a complete set of stationary-state wavefunctions, $\phi_n\ (\equiv|n\rangle)$, one can expand $\Psi(t)$ in terms of the ϕ_n's as follows:

$$\Psi(t)=\sum_{n}c_{n}(t)\exp(-E_{n}t/\hbar)\phi_{n}\equiv\sum_{n}c_{n}(t)\exp(-E_{n}t/\hbar)|n\rangle. \qquad (2)$$

Then we can obtain a formal solution of $c_k(t)$ with the help of the time-dependent perturbation theory as

$$c_{k}(t)=\left\langle k\left|P\exp\left[-\frac{i}{\hbar}\int_{0}^{t}dt'\mathscr{H}^{r}(t')\right]\right|m\right\rangle \qquad (3)$$

where P is the Dyson time-ordering operator.

On resonance condition of a $|k\rangle\leftrightarrow|m\rangle$ transition, the rotating frame Hamiltonian $\mathscr{H}^{r}(t)$ is approximately reduced to a time-independent single-transition operator for the $|k\rangle\leftrightarrow|m\rangle$ transition. Eq.(3) then indicates that the stationary wavefunction oscillates at an angular frequency $\langle k|\mathscr{H}^{r}(t)|m\rangle/\hbar$ which corresponds to the transition amplitude. The nutation frequency ω_n, therefore, is proportional to the transition amplitude. When eigenfunctions of S and M_S, $|S,M_S,I,M_I\rangle$ ($\equiv|M_S,M_I\rangle=|M_S\rangle|M_I(M_S)\rangle$), are used instead of the ϕ_n's, ω_n for an $|M_S,M_I\rangle\leftrightarrow|M_S+1,M_I'\rangle$ transition is, to first order of the perturbation treatment, given by

$$
\begin{aligned}
\omega_n &\propto \left|\langle M_S, M_I | 2\beta\mathbf{B}_1 \cdot \mathbf{g} \cdot \mathbf{S} | M_S + 1, M_I' \rangle\right| \\
&= 2\beta B_1 \left|\langle M_S | \mathbf{h}_1 \cdot \mathbf{g} \cdot \mathbf{S} | M_S + 1\rangle\right| \left|\langle M_I(M_S) | M_I'(M_S + 1)\rangle\right| \\
&= 2\beta B_1 |G| \sqrt{S(S+1) - M_S(M_S+1)} \left|\langle M_I(M_S) | M_I'(M_S + 1)\rangle\right| \qquad (4)
\end{aligned}
$$

where $|G|$ means an anisotropy of a g tensor. $|G|^2$ is given by

$$
|G|^2 = \left(\tilde{\mathbf{h}}_1 \cdot \tilde{\mathbf{g}} \cdot \mathbf{g} \cdot \mathbf{h}_1\right) - \left(\tilde{\mathbf{h}} \cdot \tilde{\mathbf{g}} \cdot \mathbf{g} \cdot \mathbf{h}_1\right)^2 / g^2 . \qquad (5)
$$

$\mathbf{B}_1$ and $\mathbf{h}_1$ stand for the applied microwave field and a unit vector in an arbitrary coordinate system, respectively. $\mathbf{h}$ stands for a unit vector of the static magnetic field of $\mathbf{B}$. Eq.(4) shows that the nutation frequency depends on the anisotropy of the g tensor, effective molecular spin quantum number, and change of nuclear spin states during its electron spin transition.

EXPERIMENTAL AND ANALYSIS

X-band cw and pulsed ESR measurements were carried out on a Bruker ESP380E spectrometer equipped with a dielectric resonator and a 1kW TWT microwave amplifier. The ESTN experiments were performed in an echo detected scheme with three pulses which consisted of nutation (microwave excitation) and π/2-π (detection) pulses. We monitored the peak of a 2-pulse Hahn echo after the nutation pulse with different pulse length (t_1). Two-dimensional (2D) ESTN spectra were constructed by sweeping the static magnetic field.

Spin Hamiltonian for *f* electrons in a cubic field

The spin Hamiltonian including interaction terms with a nuclear spin **I** is given by

$$
\begin{aligned}
\mathcal{H} &= \mathcal{H}_{eZ} + \mathcal{H}_{FS} + \mathcal{H}_{HF} + \mathcal{H}_{nZ} + \mathcal{H}_{Q} \\
&= \beta\mathbf{B} \cdot \underline{\underline{\mathbf{g}}} \cdot \mathbf{S} + \sum_{k,q} B_k^q O_k^q + \mathbf{I} \cdot \underline{\underline{\mathbf{A}}} \cdot \mathbf{S} - \beta_n \mathbf{B} \cdot \underline{\underline{\mathbf{g}}}_n \cdot \mathbf{I} + \mathbf{I} \cdot \underline{\underline{\mathbf{Q}}} \cdot \mathbf{I} \qquad (6)
\end{aligned}
$$

where $\mathcal{H}_{eZ}$, $\mathcal{H}_{FS}$, $\mathcal{H}_{HF}$, $\mathcal{H}_{nZ}$, and $\mathcal{H}_{Q}$ stand for electron Zeeman, fine structure, hyperfine coupling, nuclear Zeeman, and quadrupole terms, respectively. The fine-structure term for *f* electrons in the cubic field is derived as

$$\sum_{k,q} B_k^q O_k^q = B_4\left(O_4^0 + 5O_4^4\right) + B_6\left(O_6^0 - 21O_6^6\right) \tag{7}$$

by the crystal field theory, where O_k^q's are usual equivalent operators and B_4 and B_6 are used intead of B_4^0 and B_6^0 for simplicity, respectively. Here second order parameters (*k*=2) in the fine structure term are vanishing because of the cubic symmetry of the CaF$_2$ single crystal. For analysis of the angular dependence of conventional ESR spectra, only the electron Zeeman and fine structure terms were taken into account. Resonance fields were numerically calculated using an eigenfield method[9].

RESULTS AND DISCUSSION

Single Crystal cw-ESR Spectra of Eu^{2+} in the Octet Spin State

Fig. 1 shows a conventional cw-ESR spectrum of the Eu^{2+} ion observed at 3.5K with a magnetic field parallel to a crystallographic [111] axis of the CaF$_2$

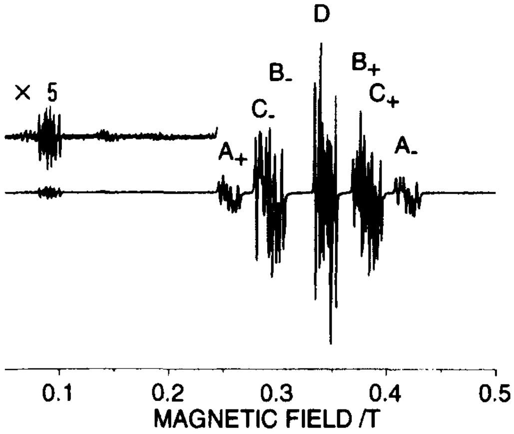

FIGURE 1 Conventional cw-ESR spectrum of Eu^{2+} in CaF$_2$.

single crystal. The observed ESR spectra consist of seven allowed transitions with complicated hyperfine structures. $A_\pm$, $B_\pm$, $C_\pm$, and D correspond to $|M_S{=}\pm7/2\rangle \leftrightarrow |\pm5/2\rangle$, $|\pm5/2\rangle \leftrightarrow |\pm3/2\rangle$, $|\pm3/2\rangle \leftrightarrow |\pm1/2\rangle$, and $|1/2\rangle \leftrightarrow |-1/2\rangle$ ESR allowed transitions, respectively. The ESR transitions of $B_\pm$ and $C_\pm$ are partly overlapped. In addition, isotopes of Eu (^{151}Eu (47.9%) and ^{153}Eu (52.1%)) complicate spectral features. The ESR spectra of the Eu^{2+} ion were analyzed using the spin Hamiltonian including the electron Zeeman and fine-structure terms in Eq.(2). From the angular dependence of ESR transitions which reflect the cubic symmetric field of the CaF_2 single crystal, we determined spin Hamiltonian parameters; $g = 1.993$, $60B_4 = -59.2\times10^{-4}$ cm^{-1}, and $1260B_6 = 0.6\times10^{-4}$ cm^{-1}. All the parameters are in agreement with previously documented ones.[8]

Electron Spin Transient Nutation Phenomena of Eu^{2+}

Fig.2 shows a contour plot of field-swept 2D-ESTN spectra of the Eu^{2+} ion

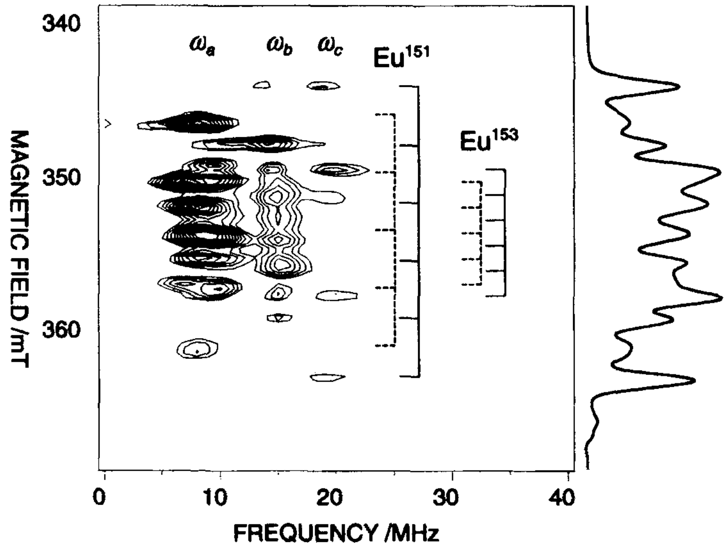

FIGURE 2 Contour plot of 2D ESTN spectrum of Eu^{2+}.

observed at 5 K in the narrow range of 339-369 mT with the magnetic field parallel to the crystallographic [111] axis. On the right of the contour plot, an echo detected field-swept ESR spectrum is given. The magnetic-field region of hyperfine ESR transitions between $|M_S{=}+1/2, M_I\rangle \leftrightarrow |M_S'{=}-1/2, M_I'\rangle$ spin sublevels were monitored. Three nutation frequencies ω_n were discriminated at 8.3 (ω_a), 14.3 (ω_b), and 19 MHz (ω_c). In this region, the nutation frequencies are affected by only the difference of nuclear spin states involved in the corresponding transitions because all the electron spin transitions are assigned to the same electron-spin transition between the $|M_S{=}+1/2\rangle$ and $|M_S'{=}-1/2\rangle$ spin sublevel. The spectral discrimination by the 2D-ESTN method simplifies the conventional ESR spectrum spectroscopically, enabling us to make facile assignments of the hyperfine lines. The observed nutation frequencies, ω_b and ω_c, are attributed to twelve hyperfine (nuclear) allowed transitions ($\Delta M_S = \pm 1$ and $\Delta M_I = 0$) and ω_a to ten nuclear forbidden transitions ($\Delta M_S = \pm 1$ and $\Delta M_I = \pm 1$) from two kinds of the isotopes as shown in Fig. 2. The allowed and forbidden hyperfine structures are indicated by solid and broken lines to first order of the perturbation theory, respectively. A quantitative feature of the nutation frequencies is discussed below.

Nutation frequencies of Eu^{2+}

The nutation frequency generally depends on the transition amplitude, being given by Eq.(4). When specific ESR transitions between M_S and M_S+1 spin sublevels are monitored, there is no difference in the dependence of the effective spin quantum numbers, S and M_S. As the g factor given by Eq.(5) depends on directions of **h** and $\mathbf{h}_1$, the nutation frequency is therefore proportional to only the change of the nuclear spin states involved in the transitions. A rotation of a nuclear spin **I** during the ESR transition from the M_S to the M_S+1 sublevel affects the nutation frequency as

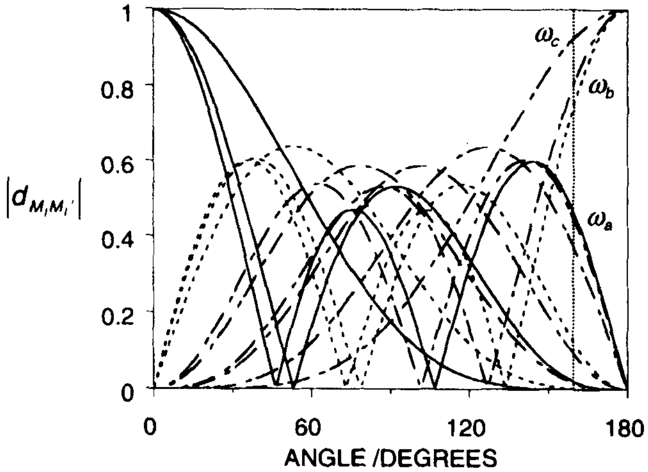

FIGURE 3 Absolute value of reduced rotation matrix elements (I=5/2)

——— $\Delta M_I=0$ ------- $|\Delta M_I|=1$ —-—- $|\Delta M_I|\geq 2$

$$\begin{aligned}\omega_{ii} &\propto \left|\langle M_I(M_S)|M_I'(M_S+1)\rangle\right| \\ &= \left|d_{M_I M_I'}(\theta)\right|\end{aligned} \tag{8}$$

where $d_{M_I M_I'}(\theta)$ is reduced rotation matrix elements, and θ is an angle between nuclear z-axes in the M_S and M_S+1 spin sublevels. The reduced rotation matrix elements are able to be calculated using the Wigner's formula.

Absolute values of the reduced rotation matrix elements for an I=5/2 nuclear spin are shown in Fig.3. If the nuclear spin is independent of electron-spin orientation, θ is zero. The reduced rotation matrix is then equal to an identity matrix:

$$d^{I=5/2}_{M_I,M_I'}(0) = \delta_{M_I,M_I'}.$$

Only hyperfine allowed transitions ($\Delta M_I = 0$) are observed. On the other hand, when the nuclear spin is affected by the electron spin ($\theta \neq 0$), hyperfine forbidden transitions ($\Delta M_I \neq 0$) are also allowed. We estimated an angle θ by comparing the ratio of the reduced rotation matrix elements with that of the observed nutation frequencies. The observed ratio is reproduced when θ is equal to about 20 and 160 degrees. In the Eu^{2+} ion case, the hyperfine interaction is much greater than the nuclear Zeeman interaction. It means that the direction of the nuclear z-axis quantized rotates during the ESR transition between $M_S=1/2$ and $M_S=-1/2$ spin sublevels. The latter angle is, therefore, the case of the Eu^{2+} ion. When θ for the $|M_S=1/2\rangle \leftrightarrow |M_S=-1/2\rangle$ ESR transition is equal to 160 degrees, θs for other fine-structure $|M_S\rangle \leftrightarrow |M_S+1\rangle$ ESR transitions are expected to be small angles on the basis of a simple vectorial consideration. The nutation frequencies for the $|M_S\rangle \leftrightarrow |M_S+1\rangle$ ESR transitions except for the $|M_S=1/2\rangle \leftrightarrow |M_S=-1/2\rangle$ ESR transition are dictated by only the change in M_S because the reduced rotation matrices for those are approximated as identity matrices due to the small θs. Our experimental results, which have not been shown here, were well interpreted by this argument.

CONCLUSIONS

The octet state of europium(II) ion has been studied by conventional cw-ESR and 2D-ESTN spectroscopy based on the pulsed ESR technique. Angular dependence of the conventional cw-ESR spectra observed was analyzed by the spin Hamiltonian with higher-order terms of S due to the cubic symmetry of the CaF_2 single crystal. The 2D-ESTN spectrum spectroscopically discriminated the hyperfine allowed ESR transitions from the hyperfine forbidden ones. Such discrimination of the ESR transitions enables us to make facile assignments of complicated ESR spectra. The nutation frequencies observed for the hyperfine allowed / forbidden transitions were quantitatively understood with the help of the reduced rotation matrix elements.

Acknowledgments

This work has been partially supported by Grants-in-Aids for Scientific

Research on Priority Area "Molecular Magnetism" (Area No. 228/04 242 103 and 04 242 105), "Delocalized Electronic Systems" (Area No. 297), and a Grant-in-Aid for Encouragement of Young Scientists (Grant No. 09 740 528 (D.S.) and 10 740 275 (K.S.)) from the Ministry of Education, Science, Sports and Culture, Japan and also by the Ministry of International Trade and Industries (NEDO project "Organic Magnets").

References

[1] J. Isoya, H. Kanda, J.R. Norris, J. Tang, and M.K. Bowman, *Phys. Rev.,* **B41,** 3905 (1990).

[2] A.V. Astashkin and A. Schweiger, *Chem. Phys. Lett.,* **174,** 595 (1990).

[3] K. Sato, D. Shiomi, T. Takui, and K. Itoh, *J. Spectrosc. Soc. Japan,* **43,**280 (1994).

[4] K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, and Y. Shirota, *J. Am. Chem. Soc.,* **119,** 6607 (1997).

[5] H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, and K. Itoh, *J. Am. Chem. Soc.,* **117,** 6376 (1995).

[6] P.G.H. Sandars and G.K. Woodgate, *Proc. Roy. Soc.,* **A257,** 269–276 (1960).

[7] J.M. Baker and F.I.B. Williams, *Proc. Roy. Soc.,* **A267,** 283–294 (1962).

[8] Y. Hayashi, M. Fukui, and H. Yoshioka, *J. Phys. Soc. Jpn.* **23,** 312–318 (1967).

[9] G.G. Belford, R.L. Belford, and J.F. Burkhalter, *J. Magn. Reson.,* **11,**251 (1973).