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Calculations of non-exponential photon-echo decays of paramagnetic ions in the superhyperfine limit

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Abstract

Photon-echo decays of several impurity paramagnetic ions are calculated. The historical average of each lattice-nuclear spin flip is described by a bivalued random-telegraph process, and the spatial average is obtained according to the crystal structure. The results are very close to that of Monte-Carlo simulations. A universal decay form is found, in agreement with the experimental observations.

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1. Introduction

In magnetic systems, spin flips of doped ions or the host lattice can cause magnetic fluctuations at the impurity ion, and a stochastic change of the transition frequency of the impurity ion. It is the main source of a doped ion's optical dephasing [1,2]. Photon echoes play a very important role in the study of optical dephasing and spectral diffusion in low temperature, and the results directly reflect the strength of the interaction between the dopant and the surrounding ions and the dynamic process. Both theories and experiments indicate that, for two-pulse photon echo, the decay can generally be expressed as $I = I_0 \exp -(4t_{12}/T_M)^x$, where t_{12} is the pulse separation and T_M is the phase storage time. Under weak magnetic field, the echo decays exponentially [3,4], with an increase of the magnetic field, it slows the spin flips in the environment [5]. As a result, T_M becomes longer, and for the paramagnetic ions with low concentration [6,7] or some ions which only have nuclear spin (Tm^{3+} [8]), the echoes clearly display non-exponential form ($x > 1$).

For the paramagnetic ions, the optical dephasing is dominated by the spin-flips between the dopant ions because of their large electron-spin magnetic moment [9]. In the low concentration sample, with an increase of the magnetic field, the population number in the upper Zeeman sublevel decreases, and the spin flips can be reduced strongly since the effective distance of the interaction becomes large [7]. When the magnetic field is very high, it can be considered as the superhyperfine limited case; the optical dephasing is induced only by the nuclear spin flips of the lattice. The large electron-mag-

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netic-moment affects the spin flips of the lattice dramatically and the rates of the flips near to the paramagnetic ion are much smaller than those of the bulk [9,10]. It seems that the spin flips form a frozen core around the impurity ion, and contribute little to the dephasing. So, as the dephasing is caused mainly by the spin flips far from the paramagnetic ion, the lattice structural details are less considered and the echo decays tend to be a universal form ($x = 2.4$) for any paramagnetic ion under a very high magnetic field [7].

The optical dephasing induced by the spin flips can be described as a stochastic process. Mims first suggested a decay form as $I = I_0 \exp - (4t_{21}/T_m)^x$ for the spin-echo problem [11]. Hu–Hartmann extended it to the optical problem [12]. In their "sudden-jump" model, the spins A (impurity ions) are independent, the environment spins B (lattice) flip randomly between two quantum states at an average rate W. Taking the spatial average of spins B, then the history average, they found that the echo decay has a non-exponential form ($x = 2$) when $Wt \ll 1$. In the calculation of the spatial average, they assumed continuous distance A–B spins and neglected the relevant lattice constants. As Devoe et al. have pointed [13], the treatment does not deal correctly with the dephasing of an ion which has only a nuclear spin. For the paramagnetic ion, it seems to be a good approximation, however the effect of frozen core is hardly taken into account.

Devoe et al. first simulated the optical dephasing in $Pr^{3+}:LaF_3$ by a Monte-Carlo method [13]. Recently, the photon-echo decays in $Er^{3+}:YLiF_4$ [10] and ruby [14] have also been simulated by the same method. The results are in good agreement with the related experiments. In these works, the history of the stochastic process was simulated by a computer generated random number.

In this paper, we use bivalued random-telegraph model to provide the average of the random history for each spin flip, an analytic expression for echo decay is obtained; then the practical lattice structure is considered for the spatial average to calculate the photon-echo decays of some paramagnetic systems. Monte-Carlo, Hu–Hartmann and our methods are compared. The effect of frozen core is discussed.

2. Theory

Under a very high magnetic field, the optical dephasing of the dilute paramagnetic ion is in the superhyperfine limit. It is completely induced by the nuclear spin flips in the host lattice. The flip–flops of the nuclear spin between two quantum states cause the stochastic fluctuation of the magnetic field at the impurity site. Let R_i be the distance between the nuclear spin i and the impurity ion, γ is the gyromagnetic ratio of the nuclear spin, and θ_i is the angle between R_i and the external magnetic field, the magnetic field changed by the flip of spin i is

$$H_{i0} = \hbar\gamma(1 - 3\cos^2\theta_i)/R_i^3, \tag{1}$$

where quantum number of the nuclear spin is $\frac{1}{2}$.

Because the quantum numbers or g-factors of a impurity ion are different in the ground and excited states, the change of the magnetic field may shift the transition frequency of the ion.

$$\Delta_i = \beta(g^*S^* - gS)H_{i0} \tag{2}$$

where S, g and S^*, g^* are the quantum number and g factor in the ground and excited states, respectively, and β is Bohr magnetic moment.

We assumed that the dephasing induced by the spin flips is independent and the dephasing induced by each spin flip can be described by a bivalued random-telegraph process. The spin flips between two possible frequency values Δ and $-\Delta$, the probabilities of taking Δ or $-\Delta$ are both $\frac{1}{2}$. The distribution of time intervals between two adjacent flips is given by $\rho(t) = W\exp(-Wt)$, and k, the number of flips within T satisfies the Poisson distribution $P_k = \exp(-WT)(WT)^k/k!$. It is well-known that the decay induced by the stochastic frequency flips can be described by a relaxation function [15] and for a two-pulse photon-echo process, the relaxation function can be expressed as:

$$\langle \exp\Phi\rangle = \langle E(t_{21})\rangle = \left\langle \exp\left[i\int_0^{t_{21}} \delta\omega(t)\,dt - i\int_{t_{21}}^{2t_{21}} \delta\omega(t')\,dt' \right]\right\rangle \tag{3}$$

and satisfies the differential equation

$$\left[\frac{\mathrm{d}^3}{\mathrm{d}t_{21}^3}+6W\frac{\mathrm{d}^2}{\mathrm{d}t_{21}^2}+(8W^2+4\Delta^2)\frac{\mathrm{d}}{\mathrm{d}t_{21}}+6W\Delta^2\right]\times\langle E(t_{21})\rangle=0,$$

$$\langle E(0)\rangle=1,\qquad \left.\frac{\mathrm{d}\langle E(t_{21})\rangle}{\mathrm{d}t_{21}}\right|_{t_{21}=0}=0,$$

$$\left.\frac{\mathrm{d}^2\langle E(t_{21})\rangle}{\mathrm{d}t_{21}^2}\right|_{t_{21}=0}=0. \tag{4}$$

The solution of these equations is [16]

$$\langle E(t_{21})\rangle=\begin{cases}\dfrac{1}{1-p^2}\left[\dfrac{1}{2}\left(1+\sqrt{1-p^2}\right)e^{-2Wt_{21}(1-\sqrt{1-p^2})}+\dfrac{1}{2}\left(1-\sqrt{1-p^2}\right)e^{-2Wt_{21}(1+\sqrt{1-p^2})}-p^2e^{-2Wt_{21}}\right] & p<1,\\ (1+2Wt_{21}+2Wt_{21}^2)e^{-2Wt_{21}} & p=1,\\ \dfrac{p^2}{p^2-1}e^{-2Wt_{21}}\left[1+\dfrac{1}{p}\sin\left(2Wt_{21}\sqrt{p^2-1}-\sin^{-1}\dfrac{1}{p}\right)\right] & p>1,\end{cases} \tag{5}$$

where $p=\Delta/W$.

At low temperatures, the spins flip mutually by the magnetic dipole–dipole interaction. Under a high magnetic field, the nonsecular interactions are quenched, the mutual-flip rate can be obtained by Fermi's golden rule. Because the paramagnetic ion has a large electron spin moment, it produces a local field at each ion of the lattice which detunes its nuclear magnetic resonance frequency from those of the unperturbed bulk ions. The local field at R_i site is

$$H_{ei}=g\beta S(1-3\cos^2\theta_i)/R_i^3. \tag{6}$$

Here we assume the population is almost in the ground state under a weak-light excitation, so the g-factor in the ground state is used. Then one can give the mutual flip rate of spin i with j as in [10]

$$W_{ij}=W_0[\Gamma^2/(D_{ij}^2+\Gamma^2)]\times[R_{nn}^6(1-3\cos^2\theta_{ij})^2/R_{ij}^6], \tag{7}$$

where R_{ij} is the distance between nuclear spins i and j, θ_{ij} is the angle between R_{ij} and the external field, Γ is the bulk nuclear magnetic resonance linewidth (HWHM), $D_{ij}=\gamma(H_{ei}-H_{ej})$ the detuning value of the resonance optical frequency, R_{nn} the distance between the nearest nuclear spins, and W_0 is the corresponding flip rate. One can find that the nuclear spins near the impurity ion have very slow flip rates and thus have a little effect on the dephasing. It is the so-called frozen core effect.

Each spin has a mutual flip with any other spin. In our calculations, W_i, the flip rate of spin i is the sum of the mutual flip rates with its neighbors, $W_i=\frac{1}{2}\sum_j^n W_{ij}$, and since each spin is taken twice, the factor $\frac{1}{2}$ is used. n is the number of neighboring spins and depends on the sample. We form the lattice by a computer, then get the parameter p for each nuclear spin in the lattice. Using Eq. (5), the echo-decay induced by each spin flip can be calculated. Taking their product we obtain the whole echo decay; N is the number of the spins in the calculations to ensure the results are independent of the lattice size.

In the following calculations, the only free parameter is W_0, which is about several kilohertz.

3. Results and discussion

We have calculated the photon-echo decays in ruby ($Al_1(-\frac{3}{2})$, $Al_1(-\frac{1}{2})$), Er^{3+}:$YLiF_4$($^4F_{9/2}\leftrightarrow{}^4I_{15/2}$, $H\parallel c$-axis and $H\perp c$-axis) and Er^{3+}:LaF_3($^4S_{3/2}\leftrightarrow{}^4I_{15/2}$). Table 1 lists the parameters used in the calculations. The crystal structures of $YLiF_4$ and LaF_3 are taken from Refs. [17,18]. The results fitted by $I=I_0\exp(-4t_{21}/T_M)^x$ are shown in Fig. 1. T_M and x compared with those of the

Table 1
The parameters used in calculations and the results (T_M and x) comparing with those of Monte-Carlo simulations and experiments

	S	g	S^*	g^*	F (kHz)	W_q (kHz)	n	N	Our results		Monte-Carlo		Experiments	
									T_M	x	T_M	x	T_M	x
Ruby[a] $R_1(-\frac{1}{2})$	$-\frac{1}{2}$	1.984	$-\frac{1}{2}$	2.445	3	5	26	1800	49 μs	2.59	34 μs	2.6	39 μs	2.6
Ruby[a] $R_1(-\frac{3}{2})$	$-\frac{3}{2}$	1.984	$-\frac{3}{2}$	2.445	3	5	26	1400	144 μs	2.59	134 μs	2.6	138 μs	2
Er^{3+}:$YLiF_4$ $H \parallel c$[c]	$\frac{1}{2}$	3	$\frac{1}{2}$	9	20	5	49	3800	11 μs	2.5	88 μs	2.6	9 μs	1.6
Er^{3+}:$YLiF_4$ $H \perp c$[d]	$\frac{1}{2}$	8.2	$\frac{1}{2}$	0	24	5	49	3800	9 μs	2.6	10 μs	2.6	10 μs	2.6
Er^{3+}:LaF_3[e]	$\frac{1}{2}$	8.03	$\frac{1}{2}$	8.2	24	4	20	3800	15 μs	2.59	–	–	17 μs	2.6

Monte-Carlo: a, b Ref. [16], c, d Ref. [10]; Experiments: a, d, e Ref. [7], b Ref. [16], c Ref. [6].

experiments and Monte-Carlo simulations are summarized in Table 1. One can find that Monte-Carlo and our methods give almost the same results, so the average of the history by computer simulation can be well expressed analytically as the product of many terms described by Eq. (3). Like the experimental observation, the samples in our calculations have a same echo decay form ($x \approx 2.6$), and T_M is close to the experimental value. But for $R_1(-\frac{1}{2})$ in ruby and Er^{3+}:$YLiF_4(H \parallel c)$, which have small g factors in the ground states, our results give much larger x values similar to Monte-Carlo simulations.

In each sample, when the g value is decreased, x gets smaller and it is same as Monte-Carlo simulation [14]. Let $g = 0$ (Hu–Hartmann model), it is not frozen core. Then the spin-flip rate is independent of the distance to the impurity ion. In ruby, Hu–Hartmann model has predicted $x = 2$, T_M is proportional to the square root of the impurity ion's effective magnetic moment $\beta(g^*S^* - gS)$ [12] and $T_M(-\frac{1}{2})/T_M(-\frac{3}{2}) = (7.6)^{1/2} = 2.76$. Table 2 lists our results in that case. x is around 2, however they are little different in various samples. Our results give $T_M(-\frac{1}{2})/T_M(-\frac{3}{2}) = 2.8$, which is very close to that of Hu–Hartmann model. So the main conclusions of the two methods are the same, in spite of the order of historical and spatial averages.

In the previous works, the ratio of T_M was estimated from the magnetic tuning rate [19]. In ruby, $T_M(-\frac{1}{2})/T_M(-\frac{3}{2}) = 7.6$, which is larger than the experimental results was explained as the effect of frozen core [4,20]. In our calculations, with frozen core, the ratio of phase memory time in ruby $T_M(-\frac{1}{2})/T_M(-\frac{3}{2}) = 2.9$ (see Table 1), which changes a little from that without frozen core, which implies that the frozen core does not affect the ratio. In fact, the dephasing in Ref. [4] was dominated by Cr–Cr spin flips and as confirmed by the later work [9] the small ratio cannot be due to frozen core. The decays in Ref. [20] were nonexponential and they separated the decays into two exponential parts so that the ratios were given from the third decay times. The ratio was about 3 which is close to our result, however, they still presumed Cr–Cr spin flips. We think that the small ratios in all cases are not due to frozen core, since one can find that the ratio is even smaller in low magnetic field than in high field. Considering linear contribution of the magnetic moment is the main reason for the large ratio 7.6 predicted by the theory.

4. Conclusion

In a very high magnetic field or low temperature, the photon-echo decay of dilute paramagnetic ion is under the superhyperfine limit, the only source of dephasing is the nuclear spin flips in the host lattice. The history of each spin flip can be well

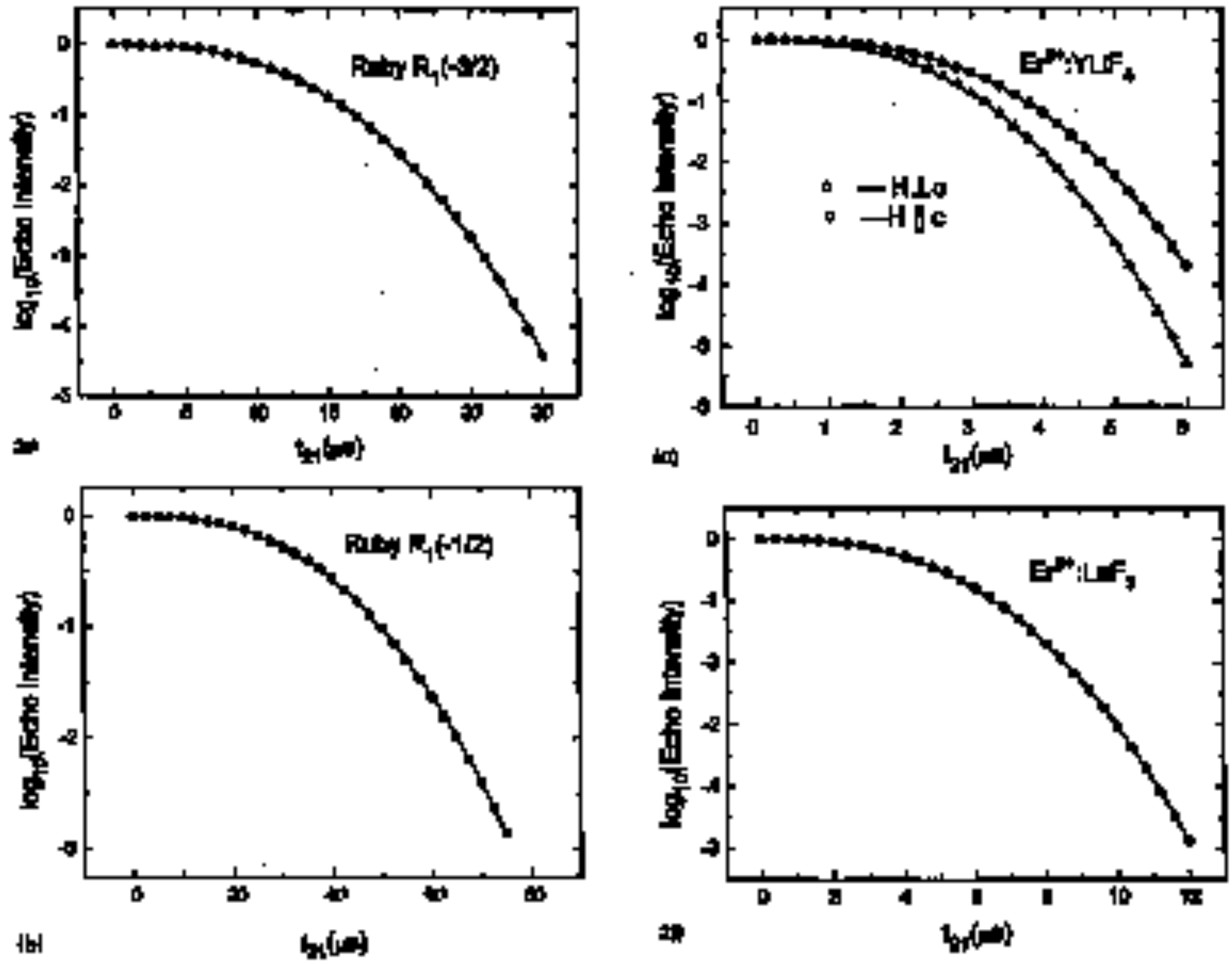

Fig. 1. Calculated results of the echo-intensity decay in ruby ($R_1(-\frac{3}{2})$, $R_1(-\frac{1}{2})$), $Er^{3+}:YLiF_4$ ($^4F_{9/2} \leftrightarrow {}^4I_{15/2}$, $H \parallel c$-axis and $H \perp c$-axis) and $Er^{3+}:LaF_3$ ($^4I_{9/2} \leftrightarrow {}^4I_{15/2}$). The solid curves are the fitted results using the form $I_0 \exp-(4t_{21}/T_m)^x$.

Table 2
Calculation results (T_m and x) without frozen core ($W_0 = 5$ kHz)

	T_m	x
Ruby $R_1(-\frac{3}{2})$	16 μs	2.1
Ruby $R_1(-\frac{1}{2})$	44 μs	1.9
$Er^{3+}:YLiF_4$ $H \parallel c$	4 μs	1.9
$Er^{3+}:YLiF_4$ $H \perp c$	3 μs	2.3

described as bivalued random-telegraph process, whose result is almost same as that of Monte-Carlo simulations. Frozen core has strong effect on the decay forms, but little on the ratio of phase memory time in a sample. Without frozen core, our calculations coincide with that of Hu–Hartmann method.

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