Magnetic Resonance and Related Phenomena

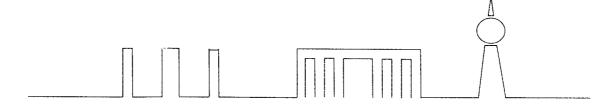
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Relaxation of Quadrupolar Spin Echoes in Ordered Magnetic Materials

S.Polulyakh¹ and N.Sergeev²

¹Simferopol State University, Simferopol 333036, Ukraine ²Institute of Physics, University of Szczecin, Szczecin 70-451, Poland

At the present time the relaxation of the spin echoes signals of a nuclei with spin I=1/2 in magnetic solids is well explained on the basis of the spectral-diffusion model of Klauder and Anderson [1-4]. In this model it is assumed that the resonance frequency of the nucleus is the time fluctuated and these fluctuations due to the temperature fluctuations of the hyperfine magnetic field at the nucleus. For the case of a quadrupolar nucleus with spin $I \geq 1$ the resonance frequency of a nucleus depends not only on the hyperfine magnetic interaction (HMI) of a nucleus, but also on the electric quadrupolar interaction (EQI) of the electric quadrupolar moment of nucleus with the inhomogeneous electric field at the site of the nucleus. In an ordered magnetic materials, with no external magnetic field, the values of HMI and EQI depend as $(3\cos^2\theta-1)$ on the direction of the electron magnetization $\mathbf{M_e}$ (θ is the angle between the direction of $\mathbf{M_e}$ and the major principal axis of HMI and EQI tensors). The time fluctuations of electron magnetization direction $\mathbf{M_e}$ produce of the time fluctuations of the angle θ and so produce of the time fluctuations of nucleus resonance frequency [5].

Assuming that the random fluctuations of the angle θ are described by the Markov stochastical process (Markov-Gauss or Markov-Lorentzian) we obtained the following expressions for the decay of the two-pulse quadrupolar echo signals at the time $t = k\tau$ (τ is the time interval between the RF pulses):

Markov - Gauss process

Markov - Lorentzian process

$$\begin{split} V(k\tau) &= V(0) \; exp \; \{ \; -6\omega_a \; sin(2\theta_0) \; \sigma_\theta \tau_c \; \big| \; 1 - \xi(m+1/2) \; \big| \; \times \\ (k-1) \; \big[\tau/\tau_c - \ln \; \big[1 + 1/(k-1) \; (1 - exp[-(k-1) \; \tau/\tau_c]) \big] \big] \} \, . \end{split}$$

In these equations τ_c is the correlation time of the time fluctuating angle θ ; $\theta_0 = \langle \theta(t) \rangle$, $\sigma_{\theta}^2 = \langle \theta^2 \rangle - \theta_0^2$ is the mean-square fluctuation of the random variable θ , ω_a is

determined by the anisotropic hyperfine field at the site of the nucleus. $\xi = C/\omega_a$, where C is the quadrupolar interaction constant of the nucleus. k is given by

$$k = 1 + [m_1 - m_2 + (\xi/2) (m_2^2 - m_1^2)] / [1 - \xi(m + 1/2)],$$

 $m, m_1, m_2 = \pm 1/2; \pm 3/2.$

From obtained expressions follows that the rates of the decay of the multiquantum echo (I=3/2) at $t=4\tau$ [6,7] and the "fractional" spin echoes [8,9] at $k\neq n$ (n is integer) exceed the relaxation rate of the Hahn echo signal at $t=2\tau$. The decay of the quadrupolar spin echoes for Markov-Lorentzian process is monotonous in the function of $lg(\tau/\tau_c)$. For the Markov-Gauss process in the dependence of the echo amplitude on $lg(\tau/\tau_c)$ a minimum is observed at $\tau \approx \tau_c$.

Good agreement between theoretical and experimental results have been obtained for chalcogenide spinels as for Hahn echo (k = 2), so for the multiquantum (k=4 [6,7]) and fractional echo signals ($k \ne n$, n is integer [8,9]).

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