TWO-FREQUENCY EXCITATION OF QUADRUPOLE SPIN ECHO

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In observations of quadrupole spin echo in the case of spins 5/2, 7/2, and 9/2, the radio-frequency pulses usually excite one of the possible transitions [1]. This produces a spin echo signal at $t = 2\tau$, where τ is the time interval between the 90 and 180° pulses.

We describe in this paper a new physical phenomenon, which comes into play when rf pulses with suitable carrier frequencies excite simultaneously several transitions, for example $|\pm 1/2\rangle \to |\pm 3/2\rangle$ and $|\pm 3/2\rangle \to |\pm 5/2\rangle$. For $I = 5/2$, at an electric field gradient asymmetry parameter $\eta = 0$, absorption is possible at the frequencies

$$\omega_1 = \frac{3}{20}\frac{eQq_{zz}}{\hbar} \text{ and } \omega_2 = \frac{3}{10}\frac{eQq_{zz}}{\hbar},$$

where eQq_{zz} is the quadrupole-interaction constant.

Assume that a sequence of two pulses with carrier frequencies ω_1 and ω_2 excite two neighboring transitions coupling the states $|\pm 1/2\rangle$, $|\pm 3/2\rangle$, and $|\pm 5/2\rangle$. In the case of single-frequency excitation of the spin system, only two states are coupled.

Under two-frequency excitation, the spin matrix [1] acquires three exponentials, whose arguments contain all three eigenvalues of the quadrupole Hamiltonian for $I = 5/2$ [2]. If the usual density-matrix formalism is used, this is equivalent to the appearance of additional echo signals, whose positions depend on the magnitude of the asymmetry parameter. Additional matrix elements, due to the coupling of the three quantum states, appear in the spin-echo matrix.

Unlike the single-frequency method, in our case the perturbation operator is

$$H_1 = -\gamma\hbar\hat{I}_x \cdot 2H_1(\cos\omega_1 t + \cos\omega_2 t), \quad (1)$$

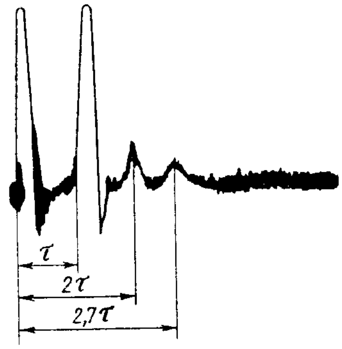
where H_1 is the amplitude of the rf field in the pulses, γ is the gyromagnetic ratio of the nucleus, and $\hat{I}_x$ is the operator of projection of the mechanical momentum of the nucleus on the X axis.

Such a perturbation induces cascaded spin transfer from the lowest level to the uppermost energy level via the intermediate state $|\pm 3/2\rangle$. It is precisely this change in the character of the perturbation operator which leads to the new mechanism of spin-echo signal production. First, the probability of the $|\pm 1/2\rangle \to |\pm 5/2\rangle$ transition becomes different from zero even for the case $\eta = 0$. In the usual single-frequency method this transition is forbidden [2].

The first pair of pulses causes precession of the magnetization vectors at the frequencies ω_1 and ω_2, with the precessing magnetizations vanishing after a time $1/\Delta\nu$, where $\Delta\nu$ is the absorption-line width. However, the second pulse pair restores the magnetization.

Whereas in the single-frequency method this restoration occurs only at the instant $t = 2\tau$, in our case the restored magnetic field can be obtained for $I = 5/2$ and $\eta = 0$ at the instants $t = 2\tau$, $3\tau/2$, 3τ, 4τ, and $5\tau/2$, since we have here two additive vector cones. The spins whose transfer to the given state is due to the action of the second exciting field have a different initial precession phase, which determines the instant of onset of phase coherence for them.

We calculated the instants of time at which the echo signals appear, the signal amplitudes, and their dependence on the pulse durations for $I = 5/2$, $7/2$, and $9/2$ in the energy representation by the density-matrix method.



Quadrupole spin echo signals of Bi^{209} nuclei in polycrystalline $BiCl_3$ at 300°K. Two-frequency action was effected for the transitions $|\pm 5/2\rangle \to |\pm 7/2\rangle$ (37.3 MHz) and $|\pm 7/2\rangle \to |\pm 9/2\rangle$ (51.7 MHz). Observation frequency 51.7 MHz. Pulse duration 18 μsec (first pulse) and 13 μsec second pulse).

Our experiment was carried out for $SbCl_3$ (Sb^{123}, $I = 7/2$) and $BiCl_3$ (Bi^{209}, $I = 9/2$). The sample was placed in a system of two coils, each of which was excited by pulse pairs from separate pulsed hf generators. Since both generators (frequencies ω_1 and ω_2) were triggered by a single pulse source, both transitions were excited simultaneously by pulses of equal duration.

The transitions excited at 300°K had frequencies 37.3 and 67.8 MHz in $SbCl_3$ and 37.3 and 51.7 MHz in $BiCl_3$. $\eta = 58\%$ for $BiCl_3$ and $\eta = 18\%$ for $SbCl_3$. The detection was at 67.8 and 51.7 MHz. When only one generator was turned on, spin echo signals were observed only at $t = 2\tau$. After the second generator was turned on and properly tuned to cover the $|\pm 1/2\rangle \to |\pm 3/2\rangle$ transition, a decrease in the intensity of the echo at $t = 2\tau$ was observed. A suitable choice of the pulse duration gave rise to additional echo signals.

Since the transitions excited in $BiCl_3$ were $|\pm 5/2\rangle \to |\pm 7/2\rangle$ and $|\pm 7/2\rangle \to |\pm 9/2\rangle$, calculation with $\eta = 0.58$ call for the echo to be observed at $t = 2\tau$, $t = 1.7\tau$, and $t = 2.7\tau$ for the $|\pm 7/2\rangle \to |\pm 9/2\rangle$ transition. Actually the signals were observed at $t = 2\tau$ and $t = 2.7\tau$ (see the figure). By varying τ it is easy to verify that the echo at 2.7τ is actually an additional one. The additional echoes disappeared when the second generator was turned off. Observation of the echo signal at $t = 1.7\tau$ is difficult at low spin-spin relaxation times. An additional echo was observed in $SbCl_3$ at $t = 3\tau/2$.

The observed effect can be used to investigate defects in crystals, since the position of the additional echo depends on η.

In conclusion, the authors thank V. Pshennikov for taking part in the construction of the two-frequency generator.

[1] T. P. Das and A. K. Saha, Phys. Rev. 98, 516 (1955).
[2] T. P. Das and E. L. Hahn, Solid State Phys., Suppl. 1 (1958).

CONDUCTION ELECTRONS WITH SMALL EFFECTIVE MASSES

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In this note we consider several effects that occur for all metals whose electronic spectrum satisfies the following two requirements: (i) Several groups of conduction electrons belonging to different energy bands correspond to the same energy ϵ. (ii) A line of degeneracy points p_0, at which $\epsilon_1(p_0) = \epsilon_2(p_0)$, exists in quasimomentum space (1 and 2 denote the numbers of the bands, $\epsilon_{1,2}(p)$ are the dispersion laws).

The surfaces $\epsilon_{1,2}(p) = \epsilon$ corresponding to this type of spectrum are made up of two cavities belonging to different bands and having a single common point $p_0(\epsilon)$ $(\epsilon_1(p_0) = \epsilon_2(p_0) = \epsilon)$. The equal-energy surface near p_0 has the form of an elliptic cone. If the vector $\vec{\xi} = \vec{H}/H$ lies inside the solid angle made up by the normals to the cone surface, then the section of the equal-energy surface by the plane p_ξ = const is closed. At small values of the difference $|\delta p_\xi| = |p_\xi - p_{0\xi}(\epsilon)|$ $(p_{0\xi}(\xi) = p_0(\epsilon)\vec{\xi})$, the intersection area $S(\epsilon, p_\xi)$ and the effective mass $m^* = (2\pi)^{-1}(\partial S/\partial\epsilon)_{p_\xi}$, which determines the conduction-electron Larmor frequency $\Omega = eH/m^*c$, take the form:

$$S(\epsilon, p_\xi) = R(\vec{\xi})(p_\xi - p_{o\xi}(\epsilon))^2, \quad m^*(\epsilon, p_\xi) = R(\vec{\xi})(p_\xi - p_{o\xi}(\epsilon))/\pi v_\xi(\epsilon), \quad v_\xi^{-1} = \frac{dp_{o\xi}}{d\epsilon} \tag{1}$$

(the dimensionless constant $R(\vec{\xi}) = 1$, and the concrete form of R is immaterial; $v_\xi(\epsilon)$ is of the order of the characteristic velocity v_0). These formulas are due to the specific nature of the dispersion law near the degeneracy point:

$$\epsilon_{1,2}(p) = \epsilon_o(p_o) + A\delta p \pm \sqrt{(B\delta p)^2 + (C\delta p)^2}, \quad (A, B, C, \approx v_o, \ \delta p = p - p_o).$$

As seen from (1), $M^* \to 0$ linearly when $p_\xi \to p_{0\xi}$.

The vanishing of the effective mass is the basis for the effects considered in what follows.

Before proceeding to further investigations, we note first that the occurrence of the line of degeneracy points can be due to certain symmetry properties of the crystal lattice of the metal. This "forced" intersection of the bands occurs, in particular, for all metals which have a nontrivial screw axis or a glide plane [1]; examples are metals with close hexagonal packing (Zn, Mg, Cd, etc.). It can be shown that the degeneracy along the line is stable, i.e., it is not lifted at small lattice deformations. It follows therefore that the