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TWO-FREQUENCY QUADRUPOLE SPIN ECHO AND ITS APPLICATIONS

V. S. GRECHISHKIN and E. M. SHISHKIN

Perm' State University

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A number of new effects in two-frequency quadrupole spin echo are observed. Thus no temperature dependence of the transverse relaxation time T_2 is detected for the additional echo signals; the latter disappear on application of an external magnetic field, and the intensity of the additional signals is strongly reduced when impurities are introduced into the sample. It is shown that two-frequency echo can be employed to study defects and detect multiplet structure in NQR spectra.

1. INTRODUCTION

FOR half-integer spins larger than 3/2, several quadrupole-energy levels can be produced in crystals[1,2]. The principle of two-frequency excitation of a quadrupole multilevel system was described by us earlier[3]. If the radio-frequency pulses act simultaneously on two neighboring transitions (for example, $\pm 1/2 \to \pm 3/2$ and $\pm 3/2 \to \pm 5/2$), then a two-frequency quadrupole spin echo is produced, characterized by the presence of additional signals not observed in the case of single-frequency excitation.

The two-frequency echo is simplest to excite experimentally with the aid of a system of crossed coils. The Hamiltonian of the radio-frequency action is taken in this case in the form

$$\mathcal{H}_1 = -2\gamma\hbar H_1 \hat{I}_x \cos\omega_1 t - 2\nu\hbar H_1 \hat{I}_y \cos\omega_2 t, \qquad (1)$$

where H_1 is the amplitude of the radio-frequency field in the pulse, ω_1 and ω_2 are the frequencies of two neighboring transitions (for $J \geq 5/2$), and $\hat{I}_x$ and $\hat{I}_y$ are the operators of the mechanical moment of the nucleus. If we disregard relaxation processes in such a system, then the calculation of the instants of time of occurrence of the spin-echo signals is easy to obtain by solving the Neumann equation for the density matrix[4]. In this case, in addition to the main spin-echo signal at $t = 2\tau$, where τ is the time interval between pulses, there are produced additional echo signals at the frequency ω_1 at the instants $t_1 = (1 + \omega_2/\omega_1)\tau$ and $t_2 = (2 + \omega_2/\omega_1)\tau$, and at the frequency ω_2 at the instants $t_1 = (1 + \omega_1/\omega_2)\tau$ and $t_2 = (2 + \omega_1 + \omega_2)\tau$.

We have investigated the properties of the two-frequency echo and obtained the regions of practical application of the observed effects.

2. SPIN-SPIN RELAXATION

The two-frequency quadrupole echo was excited with the aid of a system of crossed coils fed from two generators that produced pulses with carrier frequencies ω_1 and ω_2. The spin-echo signals from the outputs of two pulsed receivers tuned to the frequencies ω_1 and ω_2 were fed to the input of a two-beam oscilloscope. As soon as the pulse carrier frequencies entered into resonance with the frequencies of two neighboring transitions, additional echo signals at $t \neq 2\tau$ were produced in addition to the echo signals at $t = 2\tau$.

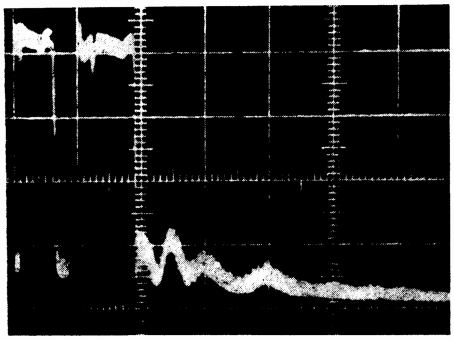

FIG. 1. Two-frequency spin-echo signals of Bi^{209} nuclei ($J = 9/2$) in $BiCl_3$ at 77°K. The first echo signal after the second pulse is produced at $t = 2\tau$; the two succeeding pulses are produced at $t_1 = 2.4\tau$ and $t_2 = 3/4\tau$. Detection of frequency 37.9 MHz; "capture" at the frequency 52.7 MHz. The experimental conditions were chosen to be favorable for the observation of all the possible signals; the durations of the first and second pulses were 100° and 60°, respectively.

The maximum induction amplitude for both transitions is observed if the pulses satisfy approximately the condition

$$90^\circ - \frac{\sqrt{13}}{2}\gamma H_1 t_w' = \frac{\pi}{2}$$

where t_w' is the pulse duration (for $J = 5/2$). To observe the additional-echo signals it is necessary that the duration of the second pulse be $t_w'' < t_w'$[3,4]. Since the optimal conditions must in any case be chosen experimentally, we do not present here the results of the simple calculations.

The object of the investigation was chosen to be $BiCl_3$[1)] (resonance of the Bi^{209} nucleus). At 77°K we had $\omega_1 = 37.9$ MHz ($\pm 5/2 \to \pm 7/2$ transition) and $\omega_2 = 52.7$ MHz ($\pm 7/2 \to \pm 9/2$ transition). Then, following two-frequency excitation, we could observe at the frequency ω_1 echo signals at the instants of time 2τ, 2.4τ, and 3.4τ, as was indeed observed experimentally (see Fig. 1). The duration of the first pulses was chosen to be 15 μsec, and that of the second 10 μsec. The spin-spin relaxation times T_2 were measured by varying τ[1]. It was observed thereby that T_2 for the main echo

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[1)] We also observed the two-frequency quadrupole echo in other crystals, for example in CdI_2, where the asymmetry parameter is equal to zero.

(instant of time 2τ) at the frequency ω_1 changes from 290 μsec at 77°K to 125 μsec at 300°K, whereas the main echo at the frequency ω_2 had $T_2 = 800$ μsec at 77°K and 200 μsec at 300°K.

The temperature dependence of T_2 is not surprising and points to a contribution of the quadrupole mechanism[5]. More surprising behavior was observed for the additional echo signals produced under the two-frequency action. Thus, the echo at the instant $t_1 = 2.4\tau$ had $T_2 \approx 50$ μsec at both 77°K and 300°K. Analogously, the echo signal produced at the instant $t_2 = 3.4\tau$ gave $T_2 = 75$ μsec. No temperature dependence of T_2 was observed for the additional echoes.

The position of the main echo signals at $t = 2\tau$ does not depend on the frequency ratio ω_2/ω_1, whereas the additional signals are functions of this ratio. We applied to the sample an external magnetic field $H_0 \sim 10$ G. The additional echo signals then vanished, whereas the signal echo at $t = 2\tau$ remained. Its intensity became even higher, since the line broadened and the echo became narrower. The introduction of the magnetic inhomogeneity can be described with the aid of an additional term in the Hamiltonian[6]:

$$\mathcal{H}_{M} = b\hbar\hat{I}_z\cos\theta, \tag{2}$$

where b is a constant, $\hat{I}_z$ is the operator of the spin momentum of the nucleus, and θ is the angle between the direction of the z axis—the gradient of the electric field—and the direction of H_0.

The external field H_0 causes a splitting of the frequencies ω_1 and ω_2, and this splitting is unequal for the different powder particles in the sample. By virtue of this, the additional echo signals disappear, since the additional signals from different powder particles are produced at different instants of time.

Thus, magnetic interactions act more strongly on the additional echo signals than on the main signals. We can therefore conclude that the T_2 for the additional echo signals are determined mainly by the magnetic dipole-dipole interactions between the nuclei. Therefore, to observe the additional echo signals it is necessary to have samples with narrow NQR lines.

The contribution of the quadrupole mechanism to the transverse relaxation for the additional echo signals is apparently small. Therefore, no temperature dependence of T_2 is observed, since the dipole-dipole interaction in the absence of disorienting motions in the lattice is practically independent of the temperature. For a quantitative explanation of the observed effects, it is necessary to develop a theory of two-frequency quadrupole spin echo with allowance for the processes of spin-spin and spin-lattice relaxation.

3. INFLUENCE OF IMPURITIES

Since the positions of the additional signals of the two-frequency echo depend on the frequency ratio ω_2/ω_1, and consequently also on the asymmetry parameter η, it follows that the effect can be used to study defects in crystals. In stationary NQR methods we cannot investigate the impurity-induced distortion of the quadrupole interaction eQq_{zz} and the asymmetry parameter η separately[1], since in that case an integral effect is observed, namely the broadening of the NQR line for both transitions.

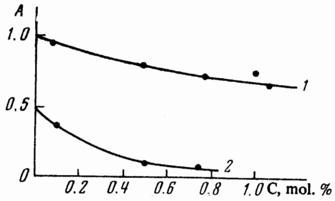

FIG. 2. Dependence of the intensity of the main echo (curve 1) and the additional echoes (curve 2) of the nuclei Bi^{209} in $BiCl_3$ on the $BiBr_3$ concentration (in molar percent).

On the other hand, when lattice defects are investigated by the two-frequency-echo method, it becomes possible to determine separately both the changes of eQq_{zz} and of η. Introduction of a $BiBr_3$ impurity into $BiCl_3$ leads to a narrowing of the echo at $t = 2\tau$ and to a broadening of the additional signals. Figure 2 shows the dependence of the echo-signal amplitude at $t = 2\tau$ (curve 1) and of the echo at $t_2 = 3.4\tau$ (curve 2) on the concentration of the $BiBr_3$ impurity at 77°K. When the $BiBr_3$ concentration become of the order of 1 molar percent, the additional echo signals could no longer be observed.

The intensity of the additional echo signals was described by the formula

$$A = A_0 e^{-NC}, \tag{3}$$

where A_0 is the intensity of the additional signal in the absence of the impurity, C the molar concentration of the impurity, and N a constant characterizing the degree of disturbance produced in the lattice of the matrix by one impurity molecule. For $BiBr_3$ in a $BiCl_3$ lattice we have $N = 276$, i.e., one molecule of $BiBr^3$ causes a frequency shift in 276 neighboring $BiCl_3$ molecules. Experiments performed with other impurities (for example with $SbCl_3$, where $N = 120$), have shown that each impurity has a different value of N.

Such experiments are more conveniently performed at the frequency ω_1, since the shift of the additional echoes is in this case larger by several times than at the frequency ω_2. On the other hand, the impurity causes a change in the ratio ω_2/ω_1 in a sphere of radius r, and this leads to a broadening of the additional echo signals. Since the position of the echo at $t = 2\tau$ does not depend on ω_2/ω_1, the influence of the impurities is much weaker here.

Thus, the two-frequency echo method is a new method for studying defects in crystals, since the change in the signal intensity makes it possible to detect easily 0.05% of impurity.

4. DETECTION OF MULTIPLET NQR SPECTRA

When observing the multiplet structure of NQR lines at the frequencies ω_1 and ω_2 (for example, owing to the non-equivalence of the resonating nuclei in the lattice), it is frequently impossible, in the single-frequency method, to relate the individual lines with one another and to determine η and eQq_{zz} correctly (this is particularly important for $J = 5/2$). The two-frequency echo can be used to identify the transitions in the presence of a multiplet line structure for $J = 5/2$.

If the spin-echo signal is observed at the frequency ω_1, then upon "capture" of the corresponding transition ω_2 by the second pair of pulses it is possible to observe the change of the intensity of the echo at $t = 2\tau$ and the appearance of the additional echoes. No such effects

ω_2, MHz	ω_1, MHz	η, %	eQq_{zz} on Sb^{121}, MHz	ω_2, MHz	ω_1, MHz	η, %	eQq_{zz} on Sb^{121}, MHz
113,762	60.870	23,5	383,36	117,581	59,000	5,3	392,14
114.380	58,035	10.7	382,14	118.408	61,998	19,2	397,60

are observed if the non-corresponding line at ω_2 is "captured." The action of the second pair of pulses on the lower transition is not manifest in any way.

The experiment was performed by us at 77°K on the nuclei Sb^{121} ($J = 5/2$) in the crystal $2SbCl_3 \cdot C_6H_5OH$. The results of the two-frequency experiment are listed in the table, where the ratio of the frequencies ω_1 and ω_2 was obtained from the "capture" effect.

It is easy to note that if the frequencies ω_1 are arranged simply in increasing order and are related to the frequencies ω_2 in the same manner as is customarily done in single-frequency procedures, then the ratios ω_1/ω_2 give entirely different values of η and eQq_{zz} for each non-equivalent position of the molecules in the lattice. Only the two-frequency method developed by us makes it possible, by using the "capture" phenomenon, to correlate the frequencies correctly in the case when $J = 5/2$. It is therefore necessary to verify the single-frequency experimental data published in the literature, since errors are possible.

In conclusion, we note that the two-frequency quadrupole echo method uncovers new possibilities in NQR.

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Note added in proof (21 June 1971). We note that application of an external magnetic field led in the case $\eta = 0$ to slow beats of all the echoes, with the exception of the main echo at the frequency ω_2.

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