# Magnetoelastic channel for nuclear-spin excitation in $FeBO_3$

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The phase-anomalous NMR signal from $^{57}Fe$ nuclei in $FeBO_3$ was investigated. The results can be explained by assuming that the magnetoelastic interaction can lead to an additional phase shift of the NMR signal relative to the RF field.

## 1. INTRODUCTION

The antiferromagnetic compound $FeBO_3$ differs significantly from other substances in its class (easy-plane antiferromagnets) by many features: it has one of the highest Néel temperatures ($T_N = 348$ K), a large magnetostriction constant $B_{15} = 3.69 \cdot 10^7$ J/m$^3$, a strong Dzyaloshinskii field $H_D \simeq 100$ kOe, rather weak sound damping (at least at frequencies lower than 100 MHz), good optical transparency, and others. These features ensure an unusual behavior of $FeBO_3$ under various conditions, particularly NMR.[1-4]

This paper is devoted to a study of the NMR features in iron borate, primarily to the anomalous values of the signal phase.

It is known that at exact resonance ($\omega = \omega_n$) the normal NMR signal is shifted in phase by $\pi/2$ relative to the exciting field $\mathbf{h}(t)$. The existence of such a shift is illustrated by Fig. 1, which shows the precession of the nuclear magnetization $\mathbf{m}$ in a coordinate frame that rotates with the field $\mathbf{h}(t)$.[5,6] In such a coordinate frame $\mathbf{h}(t)$ does not depend on the time $t$ and is described by a vector $\mathbf{H}_1 \| \mathbf{x}$ [$H_1$ is the amplitude of $\mathbf{h}(t)$].

If the motion of the nuclear magnetization $\mathbf{m}$ starts out from an equilibrium state ($\mathbf{m}_0 \| \mathbf{z}$), then the $m$ precession begins in $yz$ plane so that the transverse component $\mathbf{m}(t)$ responsible for the NMR signal has only a component along the $\mathbf{y}$ axis [$\mathbf{m}_\perp(t) \| \mathbf{y} \perp \mathbf{H}_1$], which corresponds in fact to a $\pi/2$ phase shift of $\mathbf{m}_\perp(t)$ relative to $\mathbf{h}(t)$ in an immobile coordinate frame. The anomalous NMR signal described below corresponds to a component $\mathbf{m}_{\perp a} \| \mathbf{H}_1 \| \mathbf{x}$, with $|m_x|$ commensurate with $|m_y|$.

Note that in magnetically ordered substances the anomalous NMR signal corresponding to the component $m_x$ can be due to an amplification effect,[6] wherein the hyperfine-field oscillations at the nuclei have an amplitude

$$\Delta \mathbf{H}_n(t) = A\mathbf{M}(t) = A\chi \mathbf{h}(t) = \eta \mathbf{h}(t), \tag{1}$$

much larger than the $\mathbf{h}(t)$ oscillation amplitude ($A$ is the hyperfine-interaction constant, $\mathbf{M}(t) = \chi \mathbf{h}(t)$ are the oscillations of the electron magnetization $M$ and are due to $\mathbf{h}(t)$, and $\chi$ is the magnetic susceptibility).

The gain

$$\eta = A\chi \tag{2}$$

depends on the static magnetic field $H_0$ and ranges from $10^2$ to $10^6$ ferromagnet domain walls. Damping of the oscillations $\mathbf{M}(t)$ produces between $\Delta \mathbf{H}_n(t)$ and $\mathbf{h}(t)$ a phase shift $\Delta\varphi$ defined by the relation

$$\operatorname{tg} \Delta\varphi = \delta\omega_e / (\omega_e - \omega_n), \tag{3}$$

where $\omega_e$ and $\delta\omega_e$ are the frequency and half-width of the electron magnetic (antiferromagnetic in our case) resonance.[7]

Since the oscillations of $\mathbf{m}_\perp(t)$ are phase-shifted under amplification conditions by $\pi/2$ relative to $\Delta \mathbf{H}_n(t)$ [but not $\mathbf{h}(t)$], the phase shift $\varphi$ between $\mathbf{m}_\perp(t)$ and $\mathbf{h}(t)$

$$\varphi \approx \pi/2 + \Delta\varphi, \tag{4}$$

differs from $\pi/2$. This difference, however, can be significant only where the frequencies $\omega_e$ and $\omega_n$ are superimposed $|\omega_e - \omega_n| \leqslant \delta\omega_e$. In our experiments $\omega_e \gg \omega_n$ ($\omega_e \approx 10^{11}$ s$^{-1}$, $\omega_n \approx 10^8$ s$^{-1}$ therefore

$$\Delta\varphi \approx \delta\omega_e / \omega_e \ll 1 \tag{5}$$

and the mechanism described above of formation of the anomalous NMR signal cannot explain the experimentally observed relation between the amplitude $m_x$ and the normal NMR signal amplitude $m_y$:

$$|m_x| \approx |m_y|. \tag{6}$$

We shall show below, however, that the anomalous NMR signal we observed can be explained with the aid of the magnetoelastic mechanism observed and interpreted by M. P. Petrov and associates.[3]

## 2. EXPERIMENTAL PROCEDURE AND MEASUREMENT RESULTS

We investigated the free-induction drop (FID) at a frequency $\nu = 76.445$ MHz and a temperature $T = 4.2$ K

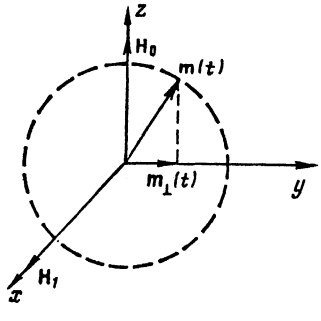


FIG. 1. Precession of nuclear magnetization $\mathbf{m}(t)$ in a coordinate frame rotating around the $z$ axis at a frequency $\omega$ at exact resonance $\omega = \omega_n$; $\omega_n$ —NMR frequency; $\mathbf{m}_\perp(t)$—transverse projection of $\mathbf{m}(t)$ under the initial condition $\mathbf{m}(0) \| z$.

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(Brooker CXP pulsed spectrometer). The rf pulse duration ($\tau_p$) was set at 2 $\mu$s and the pulse ac field was varied between $10^{-2}$ and 10 Oe.

The spectrometer quadrature-detection system has two reference-voltage channels (channels $U$ and $V$) shifted in phase by $\pi/2$. The FID signals of each channel were recorded simultaneously in different parts of the "ASPECT 2000" file. The signal phase in the $U$ channel was displayed shifted in phase by $\pi/2$ relative to the field $h(t)$. The value of $H_1$ was determined by a standard procedure with relative error $\Delta H_1/H_1 = \pm 20\%$.

Two mutual orientations of the samples relative to the fields $\mathbf{H}_0$ and $\mathbf{H}_1(t)$ were investigated. In the first $\mathbf{H}_0$ was perpendicular to $\mathbf{H}_1(t)$ and both were in the easy plane (111), while in the second $(\mathbf{H}_1 \| \mathbf{H}_0) \| (111)$.

In the $(\mathbf{H}_0 \| \mathbf{H}_1) \| (111)$ geometry the FID signal was observed only in the $U$ channel, its shape was described by a single exponential, and had an amplitude monotonic in $H_0$.

All the unusual NMR features listed above were observed only in the $(\mathbf{H}_0 \perp \mathbf{H}_1) \| (111)$ configuration, when the FID signal was observed in both channels. Figure 2 shows the FID signals in NMR $U$ and $V$ channels at different amplitudes $H_1$ of the resonant RF-field signals. At $H_1 \leqslant 1$ Oe (Fig. 2a) the NMR signal was considerably weaker in the $V$ channel than in the $U$ channel. When $H_1$ was increased to several Oe, however, the amplitudes of the NMR $U$ and $V$ signals became commensurate (Fig. 2b). It follows from Fig. 2 that the FID signal in the $U$ channel is described by a single exponential function, and that in the $V$ channel is satisfactorily approximated by two exponentials with short and long damping times, the former corresponding to damping of the magnetoelastic oscillations. The damping time of the elastic oscillations ($\tau_{mu}$), determined by known methods,[8] was $\sim 2\,\mu$s, the same as cited in Ref. 8. The magnetic-oscillations relaxation rates determined for the FID plots for the $U$ channel and for the $V$ channel (with long damping time) are comparable with $1/T_2^* \sim 50\,\mu$s determined in Ref. 9.

The dependences of the signals in channels $U$ and $V$ on the constant field $H_0$ are also different. As seen from Fig. 3, the dependences of the $U$- and $V$-signal NMR intensities on $H_0$ are the same when $H_1$ is low (Fig. 3a) and differ when $H_1$ is large (Fig. 3b).

To attenuate the magnetoelastic oscillations, the sample was coated by a thin layer of paraffin. At $H_1 = 9$ Oe this corresponds to the case illustrated in Fig. 3b, the intensity of the anomalous NMR signal was considerably weakened (Fig. 4), whereas the intensity in the $U$ channel changed little. The lower relaxation rate represented by curve *2* compared with curve *1* is due, in our opinion, to the appreciably decreased contribution of the short-lived magnetoelastic os-

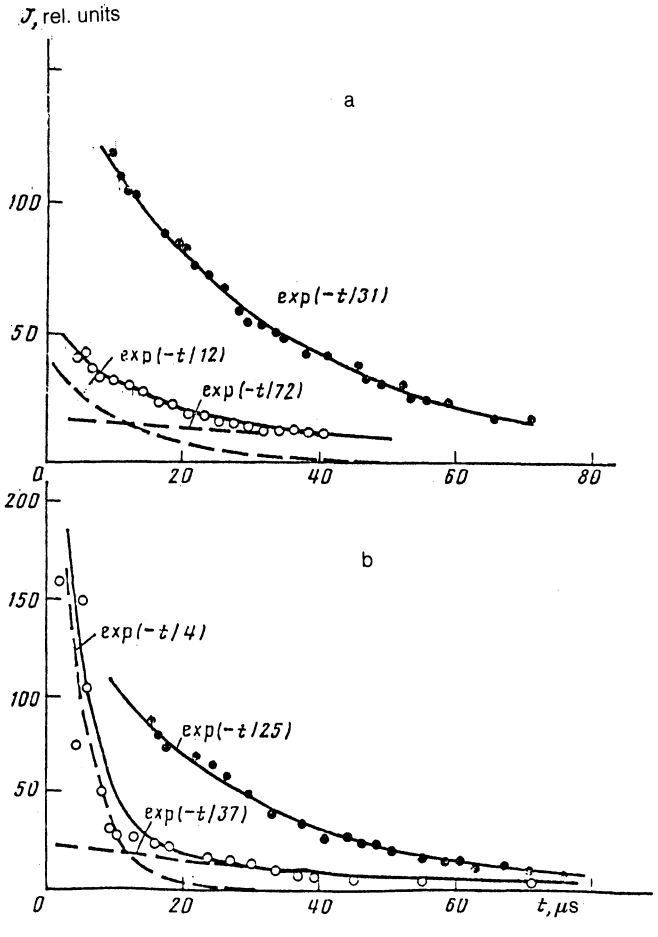


FIG. 2. Free-induction signal falloff in $U$(●) and $V$(○) channels at $H_0 = 700$ Oe. The dashed curves show the resolution into two exponents of the FIF signal in channel $V$: a) $H_1 = 0.9$ Oe; b) $H_1 = 9$ Oe.

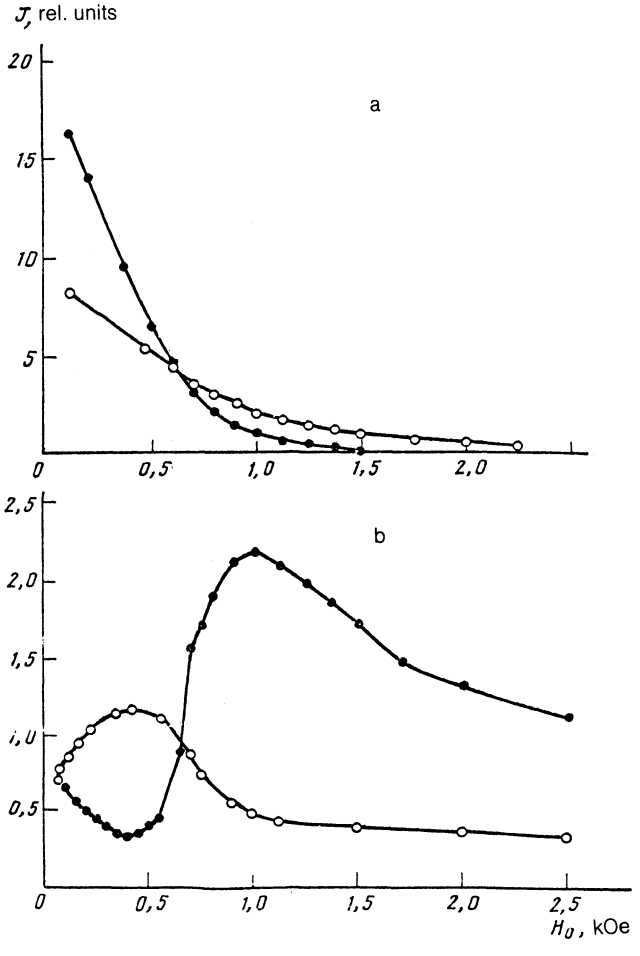


FIG. 3. $U$(●) and $V$(○) NMR signal intensities vs $H_0$: a) $H_1 = 0.9$ Oe; b) $H_1 = 9$ Oe.

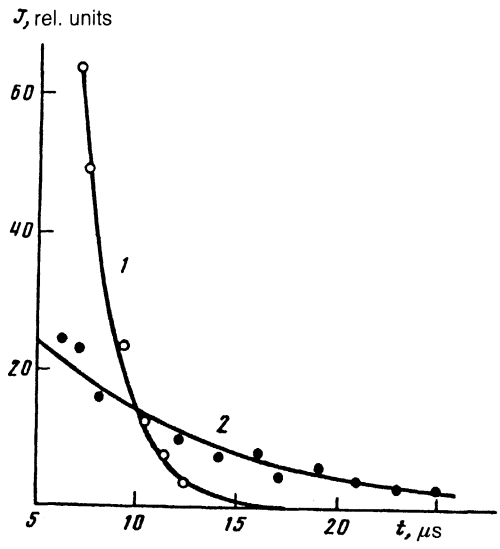


FIG. 4. Free-induction falloff signal in $V$ channel at $H_1 = 9$ Oe and $H_0 = 1500$ Oe. ○—pure sample, ■—paraffin-coated sample.

cillations, since curve *2* is described mainly by a singly exponential function.

### 3. DISCUSSION OF RESULTS

Consider the magnetoelastic mechanism of NMR-signal excitation. It is effective under several conditions, which we must list to explain the onset off the anomalous NMR $V$-signal. The first condition is excitation of sound waves $U(q,t)$ with nonzero wave vector $\mathbf{q}$ with the aid of a spatially homogeneous magnetic field $\mathbf{h}(t)$. The main obstacle to such an excitation is the wave-vector conservation law. It can be surmounted by exciting a standing wave (i.e., a pair of waves with $\mathbf{q}$ and $-\mathbf{q}$), but to this end the sample must be spatially inhomogeneous, having for example finite dimensions $L$. In particular, for a plate with normal to the $z$-axis direction the magnetization oscillations that are homogeneous in the interior of the sample can be represented by a Fourier series in the wave vectors $\mathbf{q}_n$:

$$M(t)=\sum_{n=-\infty}^{\infty} M(q_n,t)\exp(iq_nz), \tag{7}$$

where

$$q_n=\underset{L/2}{(2n+1)\pi/L}, \quad n=0,\pm1,\pm2,\ldots, \tag{8}$$

$$M(q_n,t)=\frac{1}{L}\int_{-L/2} M(t)\exp(-iq_nz)=\frac{2}{(2n+1)\pi}M(t) \tag{9}$$

are the Fourier components of the $M(t)$ oscillations; each component can excite a sound wave $U(\mathbf{q}_n,t)$ with a corresponding wave vector $\mathbf{q}_n$.

It follows from (9) that the amplitudes $M(q_n,t)$ of the harmonics decrease with increase of the number $n$, so that the efficiency of exciting the wave $U(q_n,t)$ with sufficiently large $\mathbf{q}_n$ depends also on several conditions, namely: on the magnetostriction constant $B$, on the proximity of the NMR frequencies $\omega_n$ and of the acoustic wave $\Omega(q_n) = v_0q_n$ ($v_0$ is the speed of sound), and on the sound damping. From the resonance condition

$$\omega_n=\Omega(q_n)=v_0q_n=v_0(2n+1)\pi/L \tag{10}$$

we can estimate the number $n$ of the harmonic. At $v_0 = 4\cdot10^5$ cm/s, $\omega_n = 2\pi\cdot75\cdot10^6$ s$^{-1}$ and $L = 0.2$ cm we have $n\approx31$, meaning that the amplitude (9) of the resonant harmonic $M(q_n,t)$ is 31 times weaker than the amplitude of the fundamental $M(q_0,t) = 2M(t)/\pi$. If the wave amplitude $U(q_n,t)$ is to be appreciable at such values of $n$, the constant $B$ must be large enough and the sound damping must be small. As noted at the beginning of the article, $FeBO_3$ is in both respects the most suitable easy-plane antiferromagnet. In particular, the good resolution of the acoustic-resonance lines, i.e., the inequality

$$|\Omega(q_{n+1},t)-\Omega(q_n,t)|=2\pi v_0/L\gg\delta\Omega_n, \tag{11}$$

where $\delta\Omega_n$ is resonance-line half-width, has been observed for our samples in experiment [2]. This means that each harmonic $M(q_n,t)$ excites only one acoustic harmonic, so that this excitation turns out to be the most effective.

It was stated above that the conditions listed ensure excitation of a sound wave of sufficient amplitude, but no sufficiency criterion was formulated. To this end it must be taken into account that owing to the magnetoelastic interaction the elastic oscillations $U(q_n,t)$ must be accompanied by magnetization oscillations

$$\Delta M_u(q_n,t)=\lambda U(q_n,t), \tag{12}$$

where the coefficient $\lambda$ depends on the constant $B$, on the wave vector $\mathbf{q}_n$, and on the frequency difference between the spin $[\omega_e(q_n)]$ and elastic $[\Omega(q_n)]$ waves (see, e.g., Ref. 10, p. 160). Clearly, it makes sense to take into account the magnetoelastic mechanism of nuclear-spin excitation only if the amplitude $\Delta M_u(q_n,t)$ exceeds $M(q_n,t)$(3) considerably, i.e.,

$$\Delta M_u(q_n,t)/M(q_n,t)=\eta_u(q_n)\gg1. \tag{13}$$

The condition (13) is in fact the sought criterion of sufficient effectiveness of the magnetoelastic mechanism, and it is convenient to refer to $\eta_u(q_n)$ as the magnetoelastic gain of the oscillations of the magnetization $M$. In the $FeBO_3$ samples investigated in Ref. 3 the amplitude $\Delta M_u(q_n,t)$ turn out to be larger not only than $M(q_n,t)$ (9), but also than the fundamental $M(q_0,t) = 2M(t)/\pi$ that corresponds to the $\eta_u(q_n) > (2n+1)\approx20$ value. [The samples investigated in Ref. 3 were thinner than ours, so that the resonance condition (10) corresponded to $n = 10$].

Figure 5 shows the sequence, described above, of the transformations of the oscillation energy of a uniform magnetic field $\mathbf{h}(t)$ into oscillations of electronic (**M**) as well as nuclear (**m**) magnetization. Since the amplitudes $m(q_0,t)$ and $m(q_n,t)$ are fully determined by the values of $M(q_0,t)$ and $\Delta M_u(q_n,t)$, it follows from $|M(q_0,t)|\approx|\Delta M_u(q_n,t)|$ that

$$|m(q_0,t)|\approx|m(q_n,t)|. \tag{14}$$

To clarify the nature of the anomalous NMR signal in $FeBO_3$ we must estimate not only the amplitudes $m(q_0,t)$ and $m(q_n,t)$ of the oscillations but also their phases. When

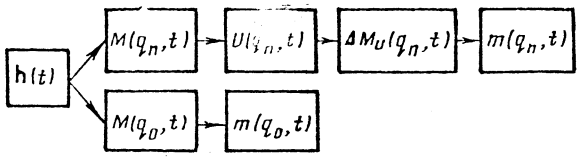


FIG. 5. Sequence of transformations of oscillations of a uniform field $\mathbf{h}(t)$ into homogeneous (with $q = q_0 = \pi/L \approx 0$) and inhomogeneous [with $q = q_n = (2n+1)\pi/L$ ] oscillations of the electron intensity $\mathbf{M}$, of the sound wave $U(\mathbf{q}_n,t)$, and of the nuclear magnetization $\mathbf{m}$.

homogeneous $m(q_0,t)$ oscillations are excited, the largest change in phase occurs during the stage of transformation of $M(q_0,t)$ and $m(q_0,t)$, when the phase shift is $\pi/2$. When the inhomogeneous $m(q_n,t)$ oscillations are excited, two substantial phase changes takes place: by $\Delta\varphi_u$ when a $u(q_n,t)$ sound wave is excited and by $\pi/2$ when the nuclear magnetization $m(q_n,t)$ is excited. The value of $\Delta\varphi_u$ is determined by a relation similar to (3):

$$\operatorname{tg}\Delta\varphi_u = \delta\Omega_n/[\omega_n - \Omega(q_n)], \tag{15}$$

where $\Omega(q_n)$ (10) and $\delta\Omega_n$ (11) are the elastic-resonance frequency and half-width introduced above for the wave vector $\mathbf{q}_n$. The quantity $\Delta\varphi$, in contrast to $\Delta\varphi$ (5) is comparable with $\pi/2$, since magnetoelastic gain takes place only near a resonance, when $|\omega_n - \Omega(q_n)| \leqslant \delta\Omega_n$. It is this quantity which determines the difference between the phases of the homogeneous $m(q_0,t)$ and inhomogeneous $m(q_n,t)$ oscillations of the nuclear magnetization.

To estimate the contribution of the harmonics $m(q_0,t)$ and $m(q_n,t)$ to the observed NMR signal it is necessary, firstly, to take into account the effect of the amplification of the NMR signals.[6] Its gist is that the oscillations of the electronic magnetization $\Delta M_m(t)$, which are due to oscillations of the nuclear magnetization $m(t)$ exceed considerably $m(t)$ in amplitude:

$$\Delta M_m(q_0,t) = \eta m(q_0,t), \quad \Delta M_m(q_n,t) = \eta m(q_n,t), \tag{16}$$

where $\eta$ is the same gain as in Eq. (2). Secondly, the magnetoelastic amplification of the component $\Delta M_m(q_n,t)$, defined by the relation

$$\Delta M_{mu}(q_n,t) = \eta_u(q_n)\Delta M_m(q_n,t) = \eta_u(q_n)\eta m(q_n,t). \tag{17}$$

Thirdly, it must be recognized that the observed NMR signal is determined by oscillations of the total magnetic moment of the sample. To calculate it we must substitute the Fourier amplitudes of the components $\Delta M_m(q_0,t)$ (16) and $\Delta M_{mu}(q_n,t)$ (17) instead of $m(q_n,t)$ (7) [in which case the left-hand side of (7) becomes dependent on $z$] and integrate over the sample volume $V$. The result is

$$\Delta M_m(t) = \Delta M_{m0}(t) \pm \Delta M_{mn}(t), \tag{18}$$

where

$$\Delta M_{m0}(t) = \int_V dr \Delta M_m(q_0,t)\exp(iq_0 z) = \frac{2}{\pi} V\eta m(q_0,t) \tag{19}$$

is the NMR signal excited via the usual electromagnetic channel, and

$$\Delta M_{mn}(t) = \int_V dr \Delta M_{mu}(q_n,t)\exp(iq_n z) = \frac{2}{(2n+1)\pi} V\eta_u(q_n)\eta m(q_n,t) \tag{20}$$

is the NMR signal excited via the magnetoelastic channel. It was shown above that $m(q_0,t)$ and $m(q_n,t)$ become comparable if $\eta_u(q_n)/(2n+1) \approx 1$. Under this condition, as follows from (19) and (20), the quantities $\Delta M_{m0}(t)$ and $\Delta M_{mn}(t)$ are also of the same order.

It is necessary next to determine the phases of the signals $\Delta M_{m0}(t)$ and $\Delta M_{mn}(t)$ to estimate their contribution to the anomalous NMR signal. Since $\Delta M_{m0}(t)$ has almost the same phase of $m(q_0,t)$, which differs by $\pi/2$ from the phase of the reference signal, it influences only the $U$-signal NMR. The $\Delta M_{mn}(t)$ phase (20) is shifted from $m(q_n,t)$ as a result of magnetoelastic amplification by $\Delta\varphi_u$ (15). Recognizing that the phases $m(q_0,t)$ and $m(q_n,t)$ also differ by $\Delta\varphi_u$, we obtain for the phase difference between the signals $\Delta M_{m0}(t)$ and $\Delta M_{mn}(t)$

$$\varphi_0 - \varphi_n = 2\Delta\varphi_u. \tag{21}$$

At exact resonance $\omega_n = \Omega(q_n)$ (10) when $\Delta\varphi_u = \pi/2$, the phase difference is $(\varphi_0 - \varphi_n) = \pi$, so that the $\Delta M_{mn}(t)$ oscillations contribute only to the $U$-signal. Exact equality of the frequencies $\omega_n$ and $\Omega(q_n)$, however, is only an accident, so that in the general case these frequencies can differ somewhat. Their difference by a half-width of the acoustic resonance $\delta\Omega_n$ yields $\Delta\varphi_n = \pi/4$, and $(\varphi_0 - \varphi_n) = \pi/2$. In this case the oscillations $\Delta M_{mn}(t)$ contribute only to the NMR $V$-signal. Since the frequency $\Omega(q_n)$ depends on the magnetic field $H_0$ via the speed of sound $V_0$ (Ref. 11), $\Delta\varphi_u$ should also depend on $H_0$. This effect ensures an additional dependence of the $V$-signal excited via the magnetoelastic channel on $H_0$ compared with the field dependence of the $U$ signal (Fig. 3b).

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