

ROLE OF DIPOLE-DIPOLE INTERACTIONS IN ACOUSTIC SATURATION OF NUCLEAR SPIN LEVELS IN CRYSTALS

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The relation between the frequency dependence of acoustic saturation of NMR signals and the acoustic nuclear resonance (ANR) line shape $g_a(\nu)$ in crystals is considered. Expressions for the acoustic saturation factor $Z_a(\nu)$ are presented which take into account the variation of the dipole-dipole interaction reservoir during saturation and yield a unique relation between $Z_a(\nu)$ and $g_a(\nu)$. Identical ANR line shape functions $g_a(\nu)$ are obtained from the experimental frequency dependence of the acoustic saturation of Na^{23} nuclei free precession signals in NaF and NaCl crystals upon excitation of ultrason quadrupole transitions with $\Delta m = \pm 2$; the widths are $\delta_a = 2.5$ kHz for NaCl and $\delta_a = 11$ kHz for NaF on a $\text{H}_0 \parallel [110]$ orientation of the external magnetic field. The dipole-dipole reservoir parameters of the crystals are calculated from the limiting saturations Z_a^{lim} obtained at various frequencies near the middle of the ANR lines. Similar experiments are carried out in the LiF crystal by radio-frequency saturation of the Li^7 nuclear precession signals. The NMR line shape function $g_a(\nu)$ derived from the saturation frequency dependence curves is identical with that measured directly with an autodyne generator. The limits of validity of the relations are discussed. Broadening of the $Z(\nu)$ curves for large saturating field amplitudes is demonstrated for the LiF crystal.

INVESTIGATIONS of acoustic nuclear resonance (ANR) are carried out most frequently using methods in which the energy levels of the nuclear spin systems are saturated with ultrasound^[1-3]. Excitation of acoustic oscillations of sufficient amplitude in the sample leads to a redistribution of the nuclear spins among the energy levels. A measure of this redistribution is the ratio of the nuclear magnetic resonance (NMR) signals before and after the action of the ultrasound.

The usual approach to the interpretation of the results is to use the kinetic equations for the changes of the individual-level populations, and yields the following expression for the acoustic saturation factor Z_a ^[1-3]:

$$Z_a = n_{st} / n_{0st} = (1 + CW_q T_1)^{-1/r}, \quad (1)$$

where n_{0st} and n_{st} are the stationary population differences of the Zeeman levels (proportional to the NMR signals) before and after the action of the ultrasound $W_q \equiv W_0 g_a(\nu)$ is the effective probability of the acoustic transitions in which the magnetic quantum number is changed by an amount $|\Delta m| \equiv q$, $g_a(\nu)$ is the form function of the acoustic resonance line, ν is the running frequency of the ultrasound, T_1 is the spin-lattice relaxation time, C is a numerical factor that depends on the nuclear spin, and $1/r$ is an exponent determined by the configuration of the acoustic field in the sample (for example, $1/r = 1$ for the case of travelling waves).

Formula (1) enables us to calculate the effective probability of the acoustic transition at the center of the ANR line. On the other hand, to obtain quantitative information on the spin-phonon interaction in a given sample it is necessary to know also the parameters of the shape function $g_a(\nu)$ of the acoustic-resonance line, for example, the width δ_a of this line. The latter

is sometimes defined as the width of the acoustic-saturation curve (i.e., as the frequency interval corresponding to half the maximum value $|1 - Z_a|_{\text{max}}$ observed at the line center), and it is this quantity which is used in the calculations and is treated as the width of the ANR line^[2]. It follows from (1), however, that the widths of the $Z_a(\nu)$ and $g_a(\nu)$ curves coincide only in the limit of infinitesimally small saturations, i.e., when $CW_q T_1 \ll 1$. With increasing transition probability W_0 , i.e., with increasing ultrasound intensity, the width of the saturation curve should increase without limit at a constant value of $g_a(\nu)$ ^[4].

The condition $CW_q T_1 \ll 1$ is never realized in the experiments, which are usually carried out at an approximate saturation 0.5. Experiment has shown that, at least in a limited range of saturations, the width of the acoustic-saturation curves depends little on the intensity of the ultrasound or remains practically constant^[5]. In this case the calculation of $g_a(\nu)$ in accordance with formula (1) at a constant width of the $Z_a(\nu)$ curve leads to errors, since this formula calls for a narrowing of the ANR line down to zero width as $W_0 \rightarrow \infty$, whereas the width of the $g_a(\nu)$ curve should be independent of the degree of saturation. Formula (1) is therefore not suitable for the calculation of the width of the $g_a(\nu)$ curve, at least for substances in which it leads to such contradictions, i.e., in particular, for crystals in which no ANR investigations by saturation methods has been made so far.

These contradictions, however, are eliminated if one uses the results of the Provotorov theory^[6,7], which takes into account effects due to the change in temperature of the dipole-dipole reservoir during the saturation process. For the case of acoustic saturation, such a calculation was performed by us earlier^[8],

and the following expression was obtained for a plane traveling ultrasonic wave¹⁾

$$Z_a = \frac{G(\Delta) + 1/CW_q T_1}{1 + G(\Delta) + 1/CW_q T_1}, \quad (2)$$

$$G(\Delta) = q^{-1} \Delta^2 \frac{4\pi^2 T_1'}{\Omega^2 T_1} = q^{-1} \Delta^2 B, \quad (3)$$

where T_1' is the relaxation time of the dipole-dipole reservoir, Ω is the "local frequency" connected with the average local field H_{loc} at the investigated nuclei by the relation $\Omega = \gamma H_{loc}$, $\Delta = \nu_0 - \nu$ is the "detuning" of the cyclic frequency of the ultrasound relative to the central frequency ν_0 of the acoustic resonance, and γ is the gyromagnetic ratio of the nucleus.

For a practical utilization of (2) it is necessary to introduce into it parameters that take into account the concrete form of the acoustic field in the sample. An analysis of this question shows that for different real field configurations (for a standing wave, an isotropic acoustic field, and also for intermediate cases, when the acoustic field is a system of interfering "quasi-standing" waves) formula (2) can be expressed with sufficient accuracy in the form

$$Z_a = \frac{G(\Delta)}{1 + G(\Delta)} + \frac{1}{[1 + G(\Delta)][1 + [1 + G(\Delta)]CW_q T_1]^{1/r}}. \quad (4)$$

It is easy to see that at $r = 1$, i.e., this formula goes over into (2) for a traveling plane wave and at $\Delta = 0$ it goes over into (1). The presence in (4) of terms that depend on the frequency of the saturating field, i.e., on Δ , leads to the experimentally observed limitation of the saturation-curve width with increasing W_q .

Under real experimental conditions with samples of relatively small size, the actual configuration of the saturating acoustic field remains unknown. This difficulty remains apparently for any sample geometry, for even in the simplest case of a wave traveling along a homogeneous cylinder the amplitudes are radially distributed over the cylinder cross section. This difficulty can be circumvented, however, by choosing the exponent $1/r$ in such a way that the experimental points $Z_a^T(W_0)$ lie on a straight line at $\Delta = 0$. Experiment shows this can always be done and that the value of r usually ranges from 1 to 3.

Formula (2) for a traveling wave or formula (4) for an arbitrary configuration of the ultrasonic field in the sample makes it possible to calculate from the saturation data not only the probability W_0 of the acoustic transitions, but also the shape function $g_a(\nu)$ of the ANR line. For this purpose, however, it is necessary to know the parameter B , which, as seen from (2), (3), and (4), can be determined from data on the limiting saturations Z_a^{lim} corresponding to the easily realized condition $CW_q T_1 \gg 1$. Then both formulas (2) and (4) yield

$$Z_a^{lim} = G(\Delta)/(1 + G(\Delta)),$$

so that $G(\Delta)$ does not depend on the configuration of the ultrasonic field and does not change with increasing ultrasound intensity at a given value of Δ . Moreover, since expression (5) does not contain the parameters of the saturating field at all, $G(\Delta)$ can be determined

in principle by any saturation of the Zeeman levels, for example, with a radio-frequency magnetic field.

Thus, to find the shape and width of the acoustic-resonance line from data on acoustic saturation it is necessary to measure the frequency dependence of the saturation factor $Z_a(\Delta)$ and to measure the limiting saturations $Z_a^{lim}(\Delta)$. Such measurements were performed by us in NaF and NaCl crystals, in which the acoustic transitions of the Na^{23} were saturated, using pulsed NMR apparatus. The investigated samples were cylinders of 12 mm diameter and 40 mm length, with plane-parallel end faces, through one of which a piezoelectric quartz converter was attached. The samples were cut along the cubic axis of the crystals and oriented with this axis perpendicular to the external magnetic field H_0 . The NMR signals were saturated at room temperature with longitudinal ultrasound of frequency $\nu \approx 7.2$ MHz, which was varied near double the Larmor precession frequency of the Na^{23} nuclei, i.e., corresponding to quadrupole transitions with $|\Delta m| = q = 2$. The ultrasonic oscillations were excited in the sample in the interval between the probing electromagnetic pulses, the repetition period of which was longer than the spin-lattice relaxation time T_1 , which was measured directly with the same setup. The frequency of the nuclear magnetic resonance was chosen in such a way that the entire range of variation of the ultrasound frequency was in the interval between neighboring peaks of the mechanical resonance of the samples. By the same token, we were able to avoid variation of the ultrasound intensity with frequency. The constancy of the ultrasonic-oscillation amplitude was additionally monitored with an electromagnetic pickup^[9].

Figure 1 shows families of acoustic-saturation curves $Z_a(\Delta)_{q=2}$ of the NMR signals of Na^{23} in NaF and NaCl single crystals, respectively, obtained at different voltages on the quartz converter, i.e., at different acoustic transitions probability densities W_0 . As seen from these figures, the width of the saturation curve remains approximately constant in a large range of saturations; this, as already noted, contradicts formula (1), which predicts a broadening of these curves with increasing saturation.

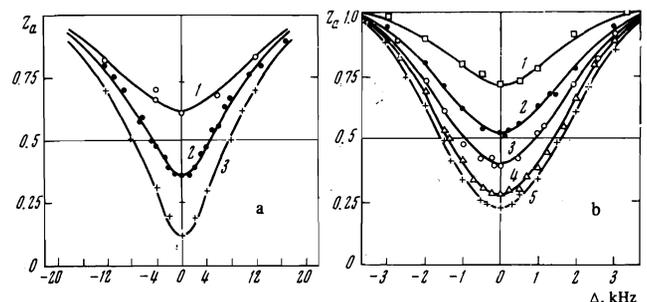


FIG. 1. Frequency dependence of the factor of acoustic saturation of the precession signals of Na^{23} nuclei in NaF and NaCl crystals at double the Larmor frequency ($\Delta m = \pm 2$) for different amplitudes of the ultrasonic deformations s_0 . a—In NaF crystal: 1— $s_0 = 3 \times 10^{-6}$, 2— $s_0 = 8 \times 10^{-6}$, 3— $s_0 = 16 \times 10^{-6}$; b—in NaCl crystal: 1— $s_0 = 10^{-6}$, 2— $s_0 = 2 \times 10^{-6}$, 3— $s_0 = 3 \times 10^{-6}$, 4— $s_0 = 4 \times 10^{-6}$, 5— $s_0 = 5 \times 10^{-6}$. The central ANR frequency ($\Delta = 0$) is $\nu_0 = 7.2$ MHz; the magnetic field H_0 is oriented along the $[110]$ axis; the longitudinal ultrasonic wave propagates along the axis $[001] \perp H_0$.

¹⁾The formula in [8] contains, in error, the factor q^2 in place of q^{-1} .

Figure 2 shows plots of the acoustic saturation factor in an NaCl crystal against the voltage applied to the piezoelectric converter at four values of the detuning Δ : ± 2.8 kHz (curve 1), -1.6 kHz (curve 2), and 0 (curve 3). In accordance with (1), all these curves should tend to zero at $W_0 \gg 1/T$. It is clearly seen in Fig. 2 that the saturation limit is different for different values of Δ , as predicted by formulas (2) and (4).

The obtained limiting values of Z_q^{lim} make it possible to calculate with the aid of formulas (5) and (3) the parameter $B = 4\pi^2 T_1' / \Omega^2 T_1$, which characterizes the properties of the dipole-dipole interaction reservoir in the given crystal. Using the experimental results of Fig. 2, we obtain for the NaCl crystal a single value $B_{\text{NaCl}} = (2.6 \pm 0.2) \times 10^{-7} \text{ sec}^2$. Analogous plots of the amplitude dependence of the acoustic-saturation factor were obtained also for the NaF crystal. A calculation of the parameter B by formula (5), using the experimental data, yielded for NaF the value $B_{\text{NaF}} = (2.8 \pm 0.2) \times 10^{-8} \text{ sec}^2$.

The results were then used to plot the corresponding shape functions $g_a(\nu)$ of the acoustic-resonance line for transitions with $|\Delta m| = 2$ with the aid of formula (4). The indicated method yielded, with good accuracy, an exponent $1/r = 1/2$ for both samples. The results of the calculation of $g_a(\nu)$ are shown in Figs. 3a for NaF and in 3b for NaCl. As seen from these figures, the functions $g_a(\nu)$ calculated from different $Z_a(\nu)$ curves practically coincide within the limits of errors and give for each crystal a single $g_a(\nu)$ curve, as should be the case by the very definition of this function.

The ANR line widths that follow from Fig. 3 are $\delta_a = 11$ kHz and 2.5 kHz for NaF and NaCl, respectively. All these data pertain to an external magnetic field H_0 parallel to the $[110]$ crystallographic axis. At the same orientation we determined also the NMR line widths by measuring the distance between the maxima and the minima of the absorption NMR derivatives recorded with an autodyne spectrometer. The values of δ determined in this case are listed in the table together with the values of δ_a and the constants B for both crystals. Attention is called to the fact that δ_a and δ are practically the same for the NaCl crystal, thus contradicting concepts based on identification of δ_a with the width of the saturation curves, according to which the acoustic line is much broader than the NMR line^[2]. In the NaF crystal, as is well known, a distinct

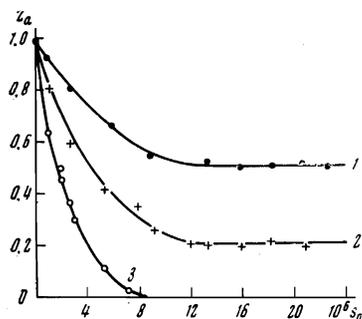


FIG. 2. Acoustic saturation factor Z_a for Na^{23} nuclei in NaCl vs the deformation amplitude s_0 at different detunings Δ of the ultrasound frequency ν relative to the central frequency ν_0 : 1— $\Delta = \pm 2.8$ kHz, 2— $\Delta = -1.6$ kHz, 3— $\Delta = 0$.

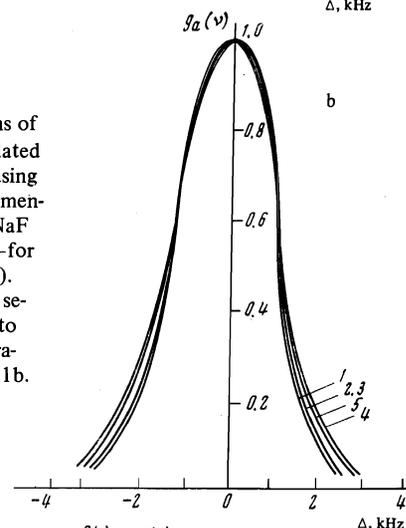
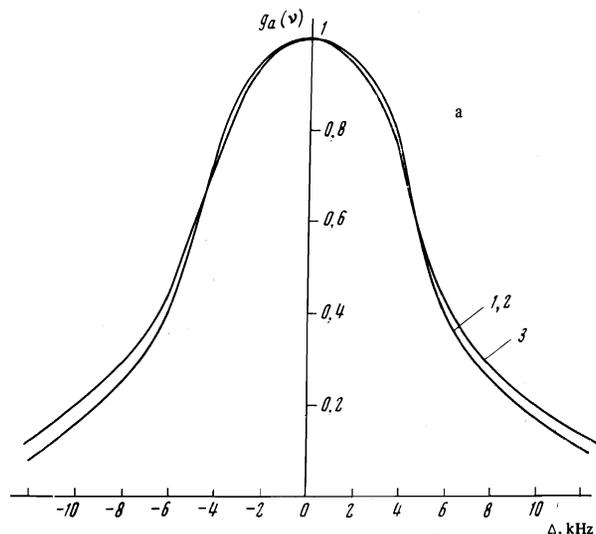


FIG. 3. Shape functions of the ANR lines $g_a(\nu)$, calculated from the curves of Fig. 1 using formula (4) and the experimental values of $G(\Delta)$: a—for NaF crystal ($\delta_a = 11.0$ kHz), b—for NaCl crystal ($\delta_a = 2.5$ kHz). The numbering of the two series of curves corresponds to the numbering of the saturation curves in Figs. 1a and 1b.

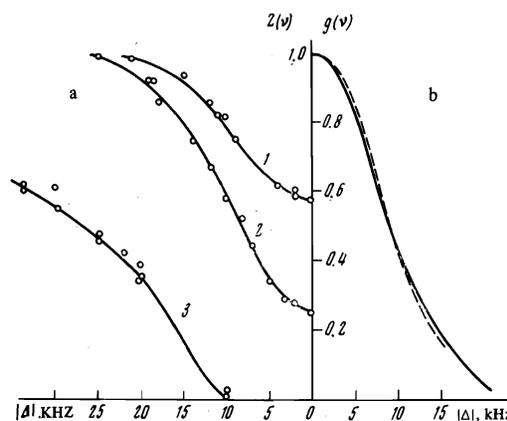


FIG. 4. Calculation of the NMR shape function $g(\nu)$ from data on the radio-frequency saturation of the precession signals of the Li^7 nuclei in the crystal LiF ($\Delta m = \pm 1$) with an external magnetic field orientation $H_0 \parallel [110]$: a—Experimental curves of frequency dependence of the saturation of the dipole transitions of Li^7 nuclei in LiF crystal, obtained for different voltages on the transmitter coil: 1—12 mV; 2—25 mV, 3—20 V; the condition (6) is violated. b—The solid curve is $g(\nu)$ calculated from the saturation curves 1 and 2 and from the limiting-saturation values; the dashed curve is the experimental $g(\nu)$ obtained by integrating the derivative signal directly registered with an autodyne oscillator at the same orientation of the external magnetic field $H_0 \parallel [110]$. The width of the two $g(\nu)$ curves is $\delta = 18$ kHz.

anisotropy of the NMR linewidth is observed^[10,5], indicating a contribution of the dipole-dipole interactions to this width. The value of δ_a obtained by us in this case is somewhat larger than δ , but this excess is also insignificant.

As a check on the reliability of the results, similar investigations were performed also on an LiF crystal by saturating the precession signals of the Li⁷ nuclei with a radio-frequency field and comparing the shape function $g(\nu)$, calculated from the saturation data, with the shape of the NMR line, which was directly measured with the aid of a Robinson autodyne oscillator at a low oscillation level. In this experiment, an alternating electric field (after several volts) with a frequency that was varied about the fundamental frequency ν_0 of the NMR, corresponding to dipole transitions of Li⁷ nuclei with $\Delta m = \pm 1$, was applied to the transmitting coil in an interval $\tau < T_1$ between the probing pulses. The investigations were likewise performed at the orientation $H_0 \parallel [110]$.

Figure 4a shows three plots of the frequency dependence of the saturation factor, Z , i.e., of the relative amplitudes of the Li⁷ precession signals, obtained for the same orientation at different voltages on the transmitting coil. In moderate saturating fields, the widths of these curves were approximately equal (about 23 kHz). Limiting saturation was obtained already at a transmitting-coil voltage on the order of 1 V. From the limiting values of Z^{lim} , obtained at different detunings Δ , we calculated the constant B , for which we obtained a value $B_{\text{LiF}} = (2.9 \pm 0.2) \times 10^{-9} \text{ sec}^2$ which agrees with the value previously obtained by investigating the solid-state effect in LiF^[11]. Using this value of B and the experimental plots of the frequency dependence of the saturation 1 and 2 (Fig. 4a) we obtained with the aid of formula (2) a single calculated $g(\nu)$ curve, which is shown by the solid line in Fig. 4b. The dashed line in the same figure shows the curve obtained by integrating the signal of the derivative of the NMR absorption, registered with an autodyne oscillator at the same orientation $H_0 \parallel [110]$. As seen from Fig. 4b, these curves agree fully, thus confirming the validity of the method described above for the calculation of the acoustic resonance form curve $g_a(\nu)$, which cannot be measured directly in saturation methods.

It must be noted, however, that the initial formula (2), obtained on the basis of Provotorov's theory, is valid under the assumption that the operator matrix element of the perturbation produced by the saturating

field is much less than the value Ω in formula (2). This corresponds to the condition $W_q \ll \gamma^2 H_{\text{loc}}^2 / \delta$ for the probabilities of the ultrasonic transitions, which is equivalent to the limitation imposed on the saturation factor by the inequality

$$Z^{-1} - 1 \ll T_1 \gamma^2 H_{\text{loc}}^2 / \delta. \quad (6)$$

Estimates show that for NaF, NaCl, and LiF crystals the condition (6) is satisfied in a wide range of saturations, up to quite appreciable values. In fields that are not very strongly saturating, however, when the inequality (6) is violated, the saturation frequency curve can broaden greatly^[7]. This effect is illustrated by the experimental curve 3 in Fig. 4a, obtained with the saturating-field amplitude much higher than the local field amplitude H_{loc} . On the other hand, in crystals with very short times T_1 and small local fields H_{loc} , the formula (2) may be violated even at relatively small saturations. This question calls for further theoretical and experimental study.

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Crystal	Nucleus	External-field orientation	$B \cdot 10^9, \text{sec}^2$	δ_a, kHz	δ, kHz
NaF	Na ²³	$H_0 \parallel [110]$	2.8 ± 0.2	11.0	9.0
NaCl	Na ²³	$H_0 \parallel [110]$	26 ± 2	2.6	2.5

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190