

ENHANCED NUCLEAR ACOUSTIC RESONANCE

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1. Introduction.

The first observation of nuclear magnetic resonance (NMR) by means of acoustic waves was made in 1955-6 [1]. The frequency used was close to 10 MHz, and the material was a single crystal of NaCl, in which each nucleus has spin $I = 3/2$. Acoustic waves have no direct interaction with a magnetic ion, and the mechanism involved was modulation by the acoustic strain of the electric quadrupole interaction.

A few years later such experiments were extended to electron paramagnetic resonance (EPR) of paramagnetic ions of the 3d group at the much higher frequency of about 10 GHz [2]. In this case the mechanism is acoustic modulation of the crystal field interaction; this acts directly only on the orbital momentum, but it is transmitted to the electron spin via the spin-orbit coupling.

In all the early work the transducers were quartz crystals, though ferromagnetic resonance in thin films of nickel has also been used [2] at 10 GHz. In the work described below, the transducer is ZnO, grown directly onto the magnetic crystal by sputter-deposition; this gives efficient transfer into the sample. If the ZnO is deposited with the c-axis normal to the surface, only longitudinal acoustic waves are generated; but if the c-axis is at an angle, transverse waves are also produced. The former are mostly used in this work, at frequencies up to about 1 GHz. Pulses of radio-frequency power of 200 ns duration are applied to the transducer, with a repetition rate of 1 kHz, the transducer being alternately switched from transmit to receive.

Two substances have been investigated, for which the parameters of the magnetic nuclear Hamiltonian have been determined by enhanced NMR. Each crystal has the tetragonal zircon structure; they are:

HoVO_4 , in which the magnetic ion is Ho^{3+} , $4f^{10}$, 5I_8 , and TmPO_4 , with Tm^{3+} , $4f^{12}$, 3H_6 .

The constants [3], [4] are:

I	Resonant frequencies MHz per Tesla			P/h
	natural	enhanced		
			⊥	
$^{165}\text{Ho } 7/2$	9.0	15	1529	26MHz
$^{169}\text{Tm } 1/2$	3.5	11	276	-

This table shows that the natural NMR frequencies are subject to very large enhancements that are extremely anisotropic. The enhancement arises as follows. For these non-Kramers ions, the tetragonal crystal field splits the manifolds to leave a singlet ground electronic state. In this, an applied magnetic field induces an electronic magnetic moment, and hence a much larger magnetic field at the nucleus is produced through the hyperfine interaction. The enhancement is large and very anisotropic because low lying states are present, to which considerable magnetic matrix elements exist for magnetic fields in the plane normal to the tetragonal axis. The constants shown have been determined by NMR measurements; the frequency is greatly increased by the enhancement, and so is the intensity for an oscillating magnetic field, normal to the steady field but still in the perpendicular plane. This field changes the electronic magnetic moment in angle, and creates an oscillating field at the nucleus through the hyperfine interaction.

2. Non-resonant acoustic absorption.

In these experiments, the acoustic velocities have been measured for all the principal modes [5], but the work on magnetic absorption has mainly involved longitudinal acoustic strains, for which the corresponding crystal field operators are:

$$[100] \quad J^{+2} + J^{-2}$$

$$[110] \quad J^{+2} - J^{-2}$$

These operators have matrix elements $\langle V \rangle$ in the

excited doublets, that occur at 21 cm^{-1} in HoVO_4 , 28 cm^{-1} in TmPO_4 . The first experiments [6] revealed the presence of non-resonant absorption, corresponding to the relation [5]

$$\alpha = [N\langle V \rangle^2 / \rho v^3 kT] [\omega^2 \tau / (1 + \omega^2 \tau^2)] \quad (1)$$

Absorption occurs only at temperatures where the doublet has a finite population N . ρ = density, v = acoustic velocity. The two levels of the doublet are driven in anti-phase through the matrix element $\langle V \rangle$ of the strain, and their relative populations change through fast relaxation to the lattice. At low field strengths this relaxation occurs mainly through an Orbach process, but at higher fields the direct process also becomes important, since its rate increases with the third power of the doublet splitting.

Measurements of the absorption at zero magnetic field over an octave of frequency, fitted to eqn (1), give an Orbach relaxation rate $1/\tau = 7(2) \times 10^9 \text{ s}^{-1}$ at $B = 0$. The absorption coefficient decreases as B rises, mainly because the doublet population diminishes, but the matrix elements and the relaxation rates also change. Nevertheless, good theoretical fits have been obtained to the variation both with magnetic field, yielding a more accurate value for the Orbach relaxation rate of $6.3(3) \times 10^9 \text{ s}^{-1}$, and with temperature. In the latter case the absorption becomes so strong that at higher temperatures no echoes are visible, and measurements were made on a dilute crystal, $(0.1\text{Ho}, 0.9\text{Y})\text{VO}_4$. The absorption coefficient is smaller by a factor ≈ 0.04 for longitudinal waves along the [110] axis than along [100], reflecting the smaller value of $\langle V \rangle^2$.

3. Resonant acoustic absorption.

Resonant absorption arises because, in the ground singlet, the acoustic strains vary the induced magnetic moment in size & direction [7]. The former changes the resonant frequency, and can be used to modulate the resonance, while the latter sets up an oscillating magnetic field that causes resonant transitions. These are of two types, quadrupolar and dipolar, that have different angular dependences. For a magnetic field B in the (001) plane that induces a moment at an angle ϕ to an acoustic wave propagated along the x -axis, the resonance intensity is a maximum for B at 45° and 135° , but zero at 0°

and 90° . The angles are interchanged for $\Delta M_I = \pm 2$ transitions. This is shown in the formulae for longitudinal acoustic waves, propagated along axes [100] and [110], respectively.

$$\begin{aligned} T^{-1} [D_1^+ v^2 \cos^2 2\phi + D_2^+ v^4 \sin^2 2\phi] \\ T^{-1} [D_1^- v^2 \sin^2 2\phi + D_2^- v^4 \cos^2 2\phi] \end{aligned} \quad (2)$$

The angular dependences have been verified experimentally, and further advantages of the acoustic method are:

(A) by measuring the decay in successive echoes, absolute measurements of absorption are obtained;

(B) the frequency can be varied over an octave in a single experiment, making possible the verification of the two different frequency dependences.

The latter arise as follows: two powers of the frequency come from the quantum $h\nu$ and the population difference ($h\nu/kT$), for $\Delta M_I = \pm 2$ transitions (the first term in each equation (2)). But for $\Delta M_I = \pm 1$ transitions there is in addition a matrix element, proportional to B and hence to ν , that gives two further powers of the frequency for the second terms in (2).

The measured absorption coefficients per metre, for HoVO_4 , are (frequency in GHz):

$$\begin{array}{lll} [100] & D_1^+ = 5.7 & D_2^+ = 950 \\ [110] & D_1^- = 0.1 & D_2^- = 17 \end{array}$$

The absorption is weaker along [110] by a factor ≈ 60 ; a similar difference is observed in TmPO_4 [8].

4. Spin-lattice relaxation.

The use of enhanced nuclear magnets for magnetic cooling was suggested by Al'tshuler, and exploited by Andres & Bucher at Bell Labs. The first NMR measurements were made in Kazan at frequencies of order 10 - 30 MHz on lanthanide ions in hydrated crystals, with low symmetry and only moderate enhancement [9]. Relaxation rates observed by recovery after saturation were found to be orders of magnitude faster than the direct process calculated by Vaisfeld (see [9]). Similar measurements of the

direct rate by Suzuki [10] for our two compounds give

HoVO ₄	7.6 MHz	30 T s ⁻¹
TmPO ₄	6.8 MHz	0.5 T s ⁻¹

The resonant absorption of acoustic waves involves same mechanism as spin-lattice relaxation by the true direct process. The relation between the two is

$$T_1^{-1}/\alpha = (16/nv^2) (kT/h)^2 (\pi \Delta\nu)$$

Here α = acoustic absorption coefficient; n the no. of ions per unit volume, v the acoustic velocity, and $\Delta\nu$ the line width parameter. From our acoustic measurements, the relaxation rates for longitudinal phonons along [100] and [110] in HoVO₄ are found to be (frequency in GHz):

$$L, [100] \quad \begin{aligned} &T[1.9 \times 10^{-8} v^2 \cos^2 2\phi \\ &+ 3.2 \times 10^{-6} v^4 \sin^2 2\phi] \end{aligned}$$

$$L, [110] \quad \begin{aligned} &T[6 \times 10^{-10} v^2 \sin^2 2\phi \\ &+ 9.0 \times 10^{-8} v^4 \cos^2 2\phi] \end{aligned}$$

At 7.6 MHz, the first term in v^2 is more important, and for the true direct process gives a rate slower by a factor 10^{-11} than observed by Suzuki. There is a similar discrepancy for TmPO₄, though here the v^2 term is absent because $I = 1/2$. Clearly, the results of Suzuki must be ascribed to paramagnetic impurities with degenerate electronic ground states (Kramers degeneracy). Our result is comparable with that of Roinel et al [11], who produced dynamic nuclear polarisation of thulium ions in TmPO₄ by "pumping" using an ytterbium impurity. At their high field (3.3 tesla), impurity effects are "frozen out", because no phonons exist of high enough frequency to flip the electronic impurity spins.

Measurements of Orbach relaxation rates show them to be comparable with the expected rates; intrinsically these are so fast, that impurities have little effect. For HoVO₄, the increase in the enhanced NMR line width up to 14 K gives a rate

$$2 \times 10^9 \exp(-30/T) \text{ s}^{-1},$$

of the same order as the rate of 6 to $7 \times 10^9 \text{ s}^{-1}$

needed to fit the non-resonant absorption.

The first acoustic experiments were carried out primarily by Andrew Briggs & John Gregg [6]; detailed measurements were made later with M.R. Wells, C.H.A. Huan, & I.D. Morris.

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