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Magnetic Resonance Absorption of Hypersonic Waves in Paramagnetic Crystals

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Magnetic resonance absorption of 9.3 kMc phonons in ruby and europium-doped calcium fluoride has been observed directly at liquid helium temperatures. The spin-lattice interaction in terms of a deformation potential has been used to calculate the transition probabilities for $\Delta M=1$ and $\Delta M=2$ transitions, both of which are allowed. The quadrupole selection rules were verified by their angular dependence. In pink ruby (0.05% Cr) the maximum attenuation observed at 1.5°K was 0.075 per cm., corresponding to a magnetoelastic constant $G^2=3\times10^{-30}$ ergs². The corresponding direct relaxation time T_{1d} is 1 sec. at 4.2°K. The experimental technique utilizes piezoelectric excitation of the hypersonic waves in a quartz crystal driven by a resonant cavity.

In the past few years, several workers have discussed the theory[1)] of spin-phonon interactions and proposed experimental investigations[2)]. Cross sections for direct spin-phonon processes were first computed by Altshuler, who predicted a measurable absorption of sound waves in crystals at electron paramagnetic resonance if the sound frequency is 10^8-10^9 cps or higher. Since the absorption cross section increases rapidly with frequency, a convenient tool to test these theories is to apply recently developed microwave frequency (10^{10} cps) sound techniques[3)] to experiments of this type. We have made such observations in ruby and in Eu-doped CaF_2.

A lattice strain representing such a hypersonic wave produces variations in the electric field gradient which, via spin-orbit coupling, then cause spin transitions. In analogy with the crystalline field term in the usual spin-Hamiltonian, we introduce the deformation tensor $d(t)$, which describes these variations, and write the phonon-spin interaction

$$\mathscr{H}(t)=S\cdot d\cdot S\,, \tag{1}$$

where S is the spin operator. In general, each component of d is a linear combination of the six strain components $\varepsilon_{kl}(t)$:

$$d_{ij}=\sum G_{ijkl}\varepsilon_{kl}\,. \qquad k,l=1,2,3 \tag{2}$$

The constants of proportionality G_{ijkl} form the magnetoelastic tensor G. By symmetry arguments the elements of this tensor can be expressed in terms of only two independent constants: $G_{1111}=G_{11}$ and $G_{2323}=G_{44}$ for cubic crystals, and four constants, $G_{11}, G_{44}, G_{12}, G_{13}$, for hexagonal and trigonal crystals. We transform the Hamiltonian $\mathscr{H}(t)$ from crystalline coordinates (x', y', z') to laboratory coordinates (x, y, z), choosing H_0 parallel to z. If H_0 is coplanar with the crystalline x', z' axes and forms an angle θ with z', the spin operator transforms as

$$S_{z'}^2=(S_z\cos\theta+S_x\sin\theta)^2\,.$$

For longitudinal waves propagating along the trigonal c-axis, the pertinent Hamiltonian terms which induce transitions in zero order are:

$$\mathscr{H}(t)=\varepsilon_{z'z'}[2(G_{11}+G_{12})-G_{13}]$$
$$\times[S_x^2\sin^2\theta+(S_zS_x+S_xS_z)\sin\theta\cos\theta]\,. \tag{3}$$

Since the operator $|S_x{}^2|$ has non-vanishing matrix elements between levels M and $M\pm2$, and $|S_zS_x+S_xS_z|$ between M and $M\pm1$, transition probabilities for $\Delta M=2$ are of the same order of magnitude as for $\Delta M=1$. They are:

$$W_{M\to M\mp1}=\frac{g(\nu)}{4h^2}\varepsilon_{z'z'}^2$$
$$\times[2(G_{11}+G_{12})-G_{13}]^2\frac{K_1}{4}\sin^2\theta\cos^2\theta\,, \tag{4a}$$

$$W_{M\to M\mp2}=\frac{g(\nu)}{4h^2}\varepsilon_{z'z'}^2$$
$$\times[2(G_{11}+G_{12})-G_{13}]^2\frac{K_2}{16}\sin^4\theta\,, \tag{4b}$$

where $g(\nu)$ is the line shape for the spin-phonon interaction and

$$K_1=(S\pm M)(S\mp M+1)(2M\mp1)^2$$

and

$$K_2=(S\pm M)(S\mp M+1)\times(S\pm M-1)(S\mp M+2)\,.$$

Similar expressions in terms of G_{11}, G_{12}, G_{13} and G_{44} can be derived for longitudinal waves traveling perpendicular to the c-axis and for transverse modes. Determination of absolute transition probabilities hinges upon measurement of ε^2, which cannot be done accurately with the present technique. However, by measuring α, the attenuation per cm, at magnetic resonance for various modes and directions of propagation one can obtain the individual constants G_{ij}. For longitudinal waves:

$$I=\frac{1}{2}\varepsilon_{z'z'}^2\rho v^3\,,$$

$$\Delta I = nh\nu W\,,$$

$$\alpha_{\Delta M=1}=\frac{\Delta I}{I}=\frac{\pi g(\nu)[2(G_{11}+G_{12})-G_{12}]^2 n\nu K_1\sin^2\theta\cos^2\theta}{4\hbar\rho v^3}\,. \qquad (5)$$

I is the phonon intensity and n is the spin population difference per cm^3. In a paramagnetic ultrasonic resonance experiment $g(\nu)$ and α are observed and thus the magnetoelastic coupling constants are measured. This results in a determination of the relaxation time due to direct spin-phonon processes[4]

$$T_{1d}=\frac{g(\nu)v^2nh}{2\alpha\nu kT}\,. \qquad (6)$$

The experimental arrangement (Fig. 1) consists of two cavities for the generation and detection of 9.4 kMc hypersonic waves in a liquid helium bath. The longitudinal waves are produced by the piezoelectric effect in the x-cut quartz crystal in the cavity on the left. The acoustic power is transmitted into the sample which is clamped between the two quartz rods with stop-cock grease as a bonding material. The transmitted power excites the cavity on the right which feeds into a sensitive radar receiver. The receiver output is connected to an integrating network, which is gated on only for the duration time of a particular pulse. The integrator puts out *dc* voltage proportional to the acoustic power, and, as the magnetic field is varied, the recorder thus traces out an acoustic power absorption line. In some experiments, a single cavity was used and the reflected power fed into the receiver by means of a circulator. Although conversion of longitudinal to transverse waves takes place at the boundaries, the latter do not contribute to the measured spin-phonon effects as long as we are in the unsaturated region. This fact has been carefully checked by varying the pulse rate (down to 20 cps) and driving power. Fig. 2 shows paramagnetic ultrasonic resonance lines in pink ruby (0.05% Cr) at $\theta=70°$ corresponding to transitions $-1/2\rightarrow+1/2$ and $-1/2\rightarrow-3/2$ (high field limit labeling). The transition probability for a pure $-1/2\rightarrow+1/2$ line should be zero

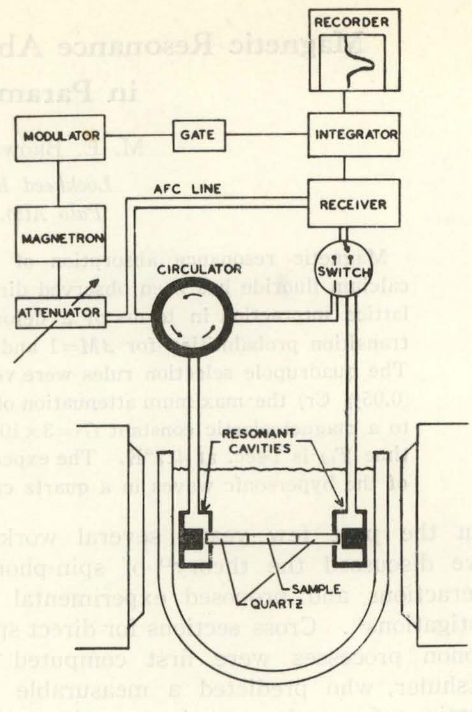
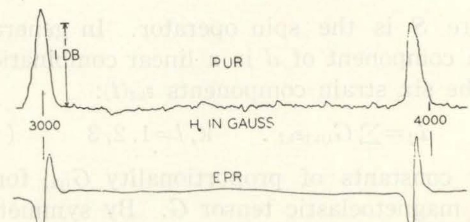


Fig. 1.



Fig, 2.

according to Eq. (4a). This does not invalidate our assumption of the quadrupolar form of the operator which describes the spin-phonon interactions, because at 9.4 Mc the wave functions are quite strongly mixed. On the contrary, when actual wave functions are taken to compute $\langle M|S_z^2|M'\rangle$, the Hamiltonian, Eq. (1), is in good agreement with experiment. Three ruby lines corresponding to $\Delta M=1$ transitions (high field labeling) were observed, but the intensity of the $\Delta M=2$ line was below our sensitivity limit. The sensitivity limit depends on the signal-to-noise ratio of the pulse received and varies from sample to sample depending mainly on face parallelism and bonding. At 1.5°K, the minimum detectable attenuation in the pink ruby studied was 2% corresponding to an attenuation $\alpha=0.0055$ per cm. The largest attenuation observed was 0.075 per cm. From this data, G^2 is computed to be 3×10^{-30} ergs^2 and $T_{1d}\simeq1$ sec at 4.2°K[4]. The latter value was obtained by using a mean sound velocity of 8×10^5 cm/sec and estimating α for transverse modes in Eq. (6).

In the event the wave front makes an appreciable angle with the detecting transducer face (a condition unfavorable for absorption detection), any velocity variation at paramagnetic ultrasonic resonace will modulate the pulse amplitude. Such line shapes with characteristically dispersive features have indeed been observed in ruby.

Attenuation of longitudinal waves was observed in cubic crystals of CaF_2 doped with 0.3% Eu. Here the sound disturbs the local cubic symmetry of the S-state ions leading to a quasi-axial term in the spin interactions. The maximum attenuation (0.12 per cm) was observed when the angle between the direction of sound propagation and magnetic field was near 45° in agreement with Eq. (4b).

Attempts to observe paramagnetic ultrasonic resonance in calcite doped with 0.1% Mn and in irradiated quartz were unsuccessful. On this basis and with our experimental sensitivity, it has been concluded that α in these crystals is less than 0.001 per centimeter.

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