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COMMUNICATIONS

Direct Detection of Aluminum-27 Resonance with a SQUID Spectrometer

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Magnetic resonance of nuclei with quadrupole and dipole splittings in the range from several kilohertz to a few megahertz has proven a difficult area of study. Traditional NQR (*1*) suffers from low sensitivity and is thus generally limited to quadrupole resonance at high transition frequencies. For lower frequencies, NQR with field cycling has been used (*2*). A recent example is aluminum-27 in alums by pulsed time-domain zero-field magnetic resonance (*3*). An alternative approach of potentially wide applicability was introduced by Jach (*4*) who obtained the quadrupole spectrum of aluminum-27 in a single crystal of α-Al_2O_3 using an RF SQUID (*s*uperconducting *qu*antum *i*nterference *d*evice) detector with linearly polarized radiation. We have constructed a sensitive *dc* SQUID spectrometer, and in this Communication we demonstrate its application using both linearly and circularly polarized radiation. In particular, we show directly detected aluminum-27 signals in both single crystal and polycrystalline Al_2O_3. The application to polycrystalline samples is crucial if low-frequency magnetic resonance with SQUID detection is to be useful for chemical studies, for example in zeolites (*5*). The application of dc SQUIDs to high-frequency NQR detection has previously been demonstrated by Hilbert *et al.* (*6*).

As a brief reminder, Jach's method relies on the transfer of zero-field quadrupolar order to Zeeman order by radiofrequency irradiation (*7*). The magnetization inherent in the Zeeman order is measured directly with a SQUID (*8*). Figure 1 shows the energy levels of ^{27}Al ($I = 5/2$) with a very low magnetic field ($\gamma B_0 \ll |e^2qQ/\hbar|$) applied along the z axis of an axially symmetric electric field gradient (*1*). At thermal equilibrium the magnetization along the field is

$$M_z = \frac{N\gamma\hbar^2}{6kT}\left[\left(\frac{35}{2}\right)\gamma B_0\right], \qquad [1]$$

where N is the number density of spins. An applied RF field will induce transitions in either the $+m$ manifold or the $-m$ manifold, depending on the polarization of the

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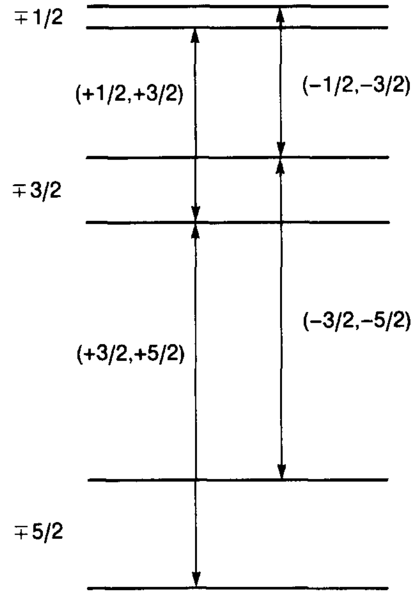

FIG. 1. Energy level diagram for ^{27}Al ($I = 5/2$), with $e^2qQ < 0$ and $\eta = 0$. A small magnetic field, with $\gamma B_0 \ll |e^2qQ/\hbar|$, is applied along the z axis of the electric field gradient to split the degeneracy of the $\pm m$ states.

radiation (7). As a saturating linearly polarized RF field is swept from low to high frequency in the vicinity of the (±3/2, ±5/2) transition, the populations of the $-3/2$ and $-5/2$ states are equalized by one rotating component of the radiation. At this point in the frequency sweep,

$$M_z = \frac{N\gamma\hbar^2}{6kT}\left[\left(\frac{34}{2}\right)\gamma B_0 + \left(\frac{3}{20}\right)\frac{|e^2qQ|}{\hbar}\right]. \qquad [2]$$

This increase in M_z, on the order of $|e^2qQ/\hbar|/\gamma B_0$, is directly detected in our SQUID spectrometer. Neglecting spin-lattice relaxation, when the RF field passes through the (+3/2, +5/2) transition the counterrotating component of the RF field should return M_z to the thermal equilibrium value of Eq. [1].

A schematic diagram of the apparatus is shown in Fig. 2. The dc magnetic field, typically about 15 gauss, is provided by flux trapped in a superconducting tube along the z axis. A radiofrequency sweeper provides the RF to a Helmholtz coil along the x axis. For the experiments requiring circularly polarized radiation, RF shifted in phase by ±90° is simultaneously applied to a similar coil along the y axis. The sample is placed in one-half of a superconducting gradiometer coil along the z axis, which is connected to the input of the SQUID. The output from the SQUID is passed through an integrator with a 5 s time constant before acquisition. A detailed description of the apparatus will be published later.

If no dc magnetic field is applied, the linearly polarized radiation would excite transitions in both the $+m$ and $-m$ manifolds at the same frequency. This would not

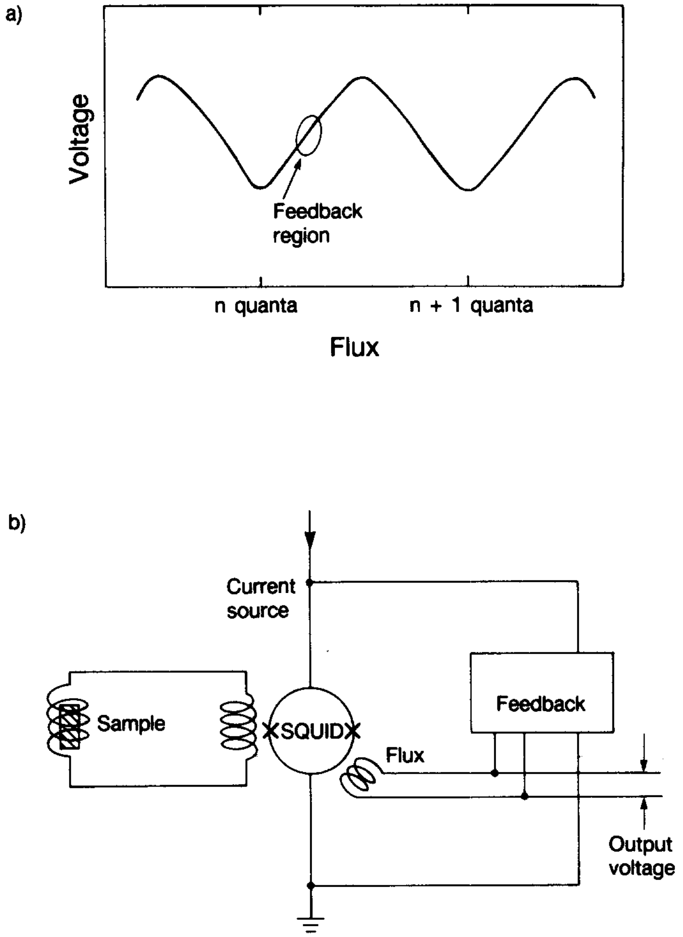

FIG. 2. (a) Voltage across the SQUID as a function of the number of flux quanta enclosed by the SQUID loop. A feedback unit applies flux to the SQUID to cancel the effect of the flux generated by the magnetization of the sample. The total flux through the SQUID remains constant, so the voltage across the SQUID is held within the encircled linear feedback region. (b) A superconducting flux transformer couples the flux from the sample into the SQUID. The output voltage of the SQUID detector is linearly proportional to the magnetization of the sample.

change the net magnetization of the spin system. Thus a magnetic field is used to split the $(-3/2, -5/2)$ and the $(+3/2, +5/2)$ transitions, allowing the linearly polarized radiation to be frequency selective in exciting transitions. In zero field, any magnetization induced by circularly polarized radiation is rapidly quenched by cross-relaxation between the $\pm m$ manifolds.

In Fig. 3 we show the spectrum of single crystal α-Al_2O_3 obtained with linearly polarized RF, similar to that previously published by Jach. The frequencies at which the $(\pm 1/2, \pm 3/2)$ and $(\pm 3/2, \pm 5/2)$ transitions occur give the quadrupole coupling

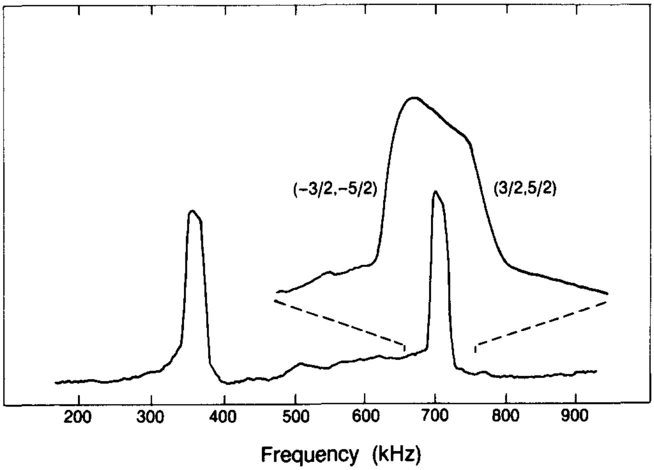

FIG. 3. Magnetization induced along the electric field gradient z axis of a single crystal of α-Al_2O_3, as a weak linearly polarized RF field is swept from low to high frequency. The inset shows a detailed view of the ($\pm 3/2$, $\pm 5/2$) transitions during a slower sweep. The asymmetric lineshape is due to spin–lattice relaxation during the sweep.

constant and asymmetry parameter, $e^2qQ/\hbar = 2.39 \pm 0.01$ MHz and $\eta = 0.0$, reflecting the relatively high symmetry of the octahedral aluminum site. This is in excellent agreement with previous work reporting $e^2qQ/\hbar = 2.393$ MHz (*1*).

An experiment was also performed with circularly polarized radiation, selectively exciting transitions among either the $+m$ or the $-m$ manifold, depending on the sense

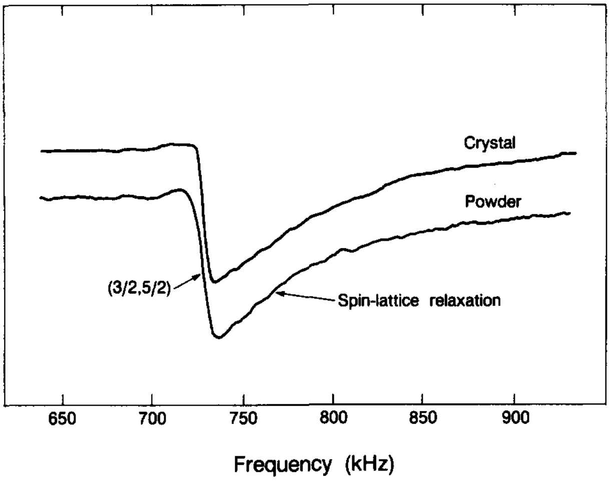

FIG. 4. Response of single crystal and powder samples of Al_2O_3 using circularly polarized radiation. Shown is the SQUID-detected magnetization induced by selectively exciting the (3/2, 5/2) transition, and an exponential decay of the magnetization back to the thermal equilibrium value.

of polarization. Figure 4 shows results as the frequency of circularly polarized RF is swept through the (±3/2, ±5/2) transition. The RF does not have the proper polarization to induce transitions between (−3/2, −5/2) and we then observe a selective excitation of (3/2, 5/2) and an exponential decay of M_z back to its thermal equilibrium value after passing through resonance. The spin–lattice relaxation is observed directly from the decay in Fig. 4, yielding $T_1 = 85 \pm 5$ s. As shown in the lower trace of Fig. 4, similar results are obtained from a polycrystalline sample of α-Al_2O_3.

Conventional NMR detectors are based on Faraday's law, so the measured voltage is proportional to the oscillation frequency of the magnetization. This frequency dependence of the voltage severely reduces the sensitivity of a Faraday detector when it is used to measure a very slowly changing magnetization. The dc SQUID (*9*), on the other hand, is an ultra-low noise detector which directly measures magnetic field, not voltage, and is not based on Faraday's law. The magnitude of the signal is therefore independent of the frequency of the oscillating magnetization, and such a SQUID detector is ideally suited for measuring induced magnetization in low-frequency magnetic resonance. Experiments are currently under way using our SQUID spectrometer for other samples, including aluminum-containing minerals and catalysts.

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