NUCLEAR MAGNETIC RESONANCE IN THE PURE QUADRUPOLE REGIME*

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In a solid-state environment in which a half-integer-spin nucleus ($I \geq \frac{3}{2}$) experiences very strong electric quadrupole coupling, conventional nuclear magnetic resonance (nmr) utilizing polycrystalline (powder) specimens is not feasible at typical magnetic field strengths such that the Larmor frequency, $\nu_L = \gamma H/2\pi$, remains always significantly smaller than the characteristic quadrupole frequency, $\nu_Q = 3e^2qQ/2I(2I-1)h$. The point of this Letter is to report the feasibility and value of observing an unconventional nmr in polycrystalline samples at roughly twice the Larmor frequency despite the condition $\nu_L < \nu_Q$. Good estimates of the quadrupole coupling and the effective gyromagnetic ratio may be obtained from measurements made entirely in the conventional nmr frequency domain. Since the resonance condition is only first affected by the quadrupole coupling in third order, the initial search for resonance need cover a relatively narrow frequency range.

Figure 1 shows the usual energy-level diagram and transitions for the Zeeman effect of the nuclear quadrupole resonance for $I = \frac{3}{2}$. The customary Zeeman-effect transitions occur in the vicinity of the characteristic quadrupole frequency, $\nu_Q = e^2qQ/2h$, whereas we are now interested in the transition between the $\pm\frac{1}{2}$ levels (quadrupole states labeling) which reduces to zero frequency when the magnetic field is reduced to zero. For axially symmetric electric field gradient ($\eta = 0$), the resonance frequency of this transition in the single-crystal case is given to first order in the applied field H by[1]

$$\nu = (\gamma H/2\pi)[\cos^2\theta + 4\sin^2\theta]^{1/2}, \qquad (1)$$

where θ is the angle between the applied field and the z axis of the field-gradient tensor. The effective γ of this transition varies smoothly from 1 at $\theta = 0°$ to 2 at $\theta = 90°$ (Fig. 1).

For a polycrystalline specimen, the intensity distribution envelope of resonance frequencies, averaged over all crystallite orientations, is determined by[2]

$$I(\cos\theta) \sim \left|\frac{d\nu}{d(\cos\theta)}\right|^{-1} \sim \left|\frac{(4-3\cos^2\theta)^{1/2}}{3\cos\theta}\right|. \qquad (2)$$

Aside from the factor $(4-3\cos^2\theta)^{1/2}$, this distribution is the same as those encountered in the case of the first-order quadrupole satellite lines in nmr[2] and in the case of axially symmetric, anisotropic Knight shift broadening of the nmr in noncubic metals.[3] In a powder specimen, a resonance is to be expected at the frequency corresponding to the singularity in $I(\cos\theta)$ which occurs when $\cos\theta = 0$. To first order in H, this frequency will be

$$\nu_2 = 2(\gamma H/2\pi) = 2\nu_L. \qquad (3)$$

The energy-level expressions for $I = \frac{3}{2}$ are readily obtained in closed form when $\eta = 0$ and $\cos\theta = 0$ by solving the secular equation.[4] The exact expression for the frequency corresponding to (3) is then

$$\nu_2 = \nu_L + \tfrac{1}{2}[(\nu_Q + 2\nu_L)^2 - 2\nu_Q\nu_L]^{1/2} - \tfrac{1}{2}[(\nu_Q - 2\nu_L)^2 + 2\nu_Q\nu_L]^{1/2}. \qquad (4)$$

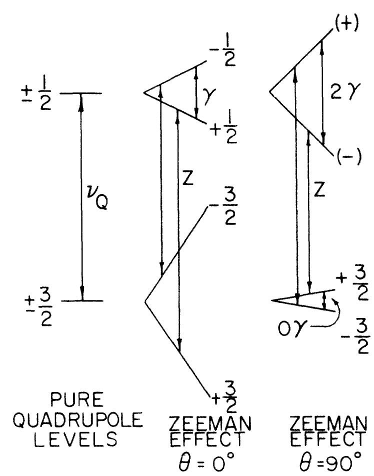

FIG. 1. Zeeman splitting of the nuclear-quadrupole energy levels, showing the conventional Zeeman-effect transitions (Z) and the magnetic transitions (0γ, γ, and 2γ) which reduce to zero frequency when H goes to zero. θ is the angle between the applied field H and the z axis of the field-gradient tensor. The $+\frac{3}{2}$ and $-\frac{3}{2}$ levels in the $\theta = 90°$ case are actually not "pure", as indicated; however, the extent of admixture of other states is very weak compared to the mixing of the $\pm\frac{1}{2}$ levels, the degeneracy of the $\pm\frac{3}{2}$ levels only being lifted in third order.

Expansion of (4) under the condition that $\nu_L \ll \nu_Q$ yields an approximate expression for the transition frequency (to third order in H),

$$\nu_2 = 2\nu_L[1-\tfrac{3}{4}(\nu_L/\nu_Q)^2], \qquad (5)$$

which indicates more clearly than (4) that the effect of the quadrupole coupling is to pull the resonance condition toward a lower effective γ, away from the 2γ condition of (3). This effect continues until at sufficiently large magnetic field strengths, $\nu_L \gg \nu_Q$, the resonance (4) becomes the high-frequency quadrupole satellite line of the magnetic resonance spectrum with an effective γ of just γ, rather than 2γ. Since the resonance condition (4) does not depend on the quadrupole coupling in first order as do the conventional Zeeman-effect transitions, field-gradient inhomogeneities may be expected to have relatively little effect in smearing out this resonance.

We have observed these "double Larmor frequency" resonances for a number of spin-$\frac{3}{2}$ nuclei in cases where the field gradient is axially symmetric. A Varian Associates wide-line nmr spectrometer was used, providing resonance frequencies in the range 2-16 Mc/sec. The quadrupole couplings and effective γ values were determined by fitting the exact expression for the frequency (4) to the measured frequency-versus-field behavior of the resonance. Figure 2 shows two examples of frequency-versus-field plots of this type. In Fig. 2(a) is shown the case of Cu^{65} in cuprous oxide, Cu_2O. The fit of (4) to the data points yields $\nu_Q = 26.15$ Mc/sec and $\gamma/2\pi = 1.1284$ Mc/kOe (at 300°K). These may be compared with the ν_Q value measured[5] by conventional pure quadrupole resonance of 25.99 Mc/sec and the accepted Cu^{65} gyromagnetic ratio of 1.1285 Mc/kOe. In Fig. 2(b) is shown the case of Cl^{35} in potassium hexachlororhenate, K_2ReCl_6. The fit of (4) to the data points yields $\nu_Q = 13.83$ Mc/sec and $\gamma/2\pi = 0.421\,07$ Mc/sec kOe, which may be compared with $\nu_Q = 13.89$ Mc/sec from pure quadrupole spectroscopy,[6] and $\gamma/2\pi = 0.4172$ Mc/sec kOe for the Cl^- ion. In this case, the departure of $\gamma/2\pi$ from the free-ion value results from a paramagnetic shift contribution. Taking account of magnetic shift effects in the energy-level calculation causes γ in (4) to be replaced by $\gamma(1+\sigma_\perp)$, where $\sigma_\perp$ is the perpendicular component of the magnetic shift tensor. In the case of K_2ReCl_6, we then have that $\sigma_\perp = +0.93\,\%$ (at 300°K). These results clearly indicate that useful measurements of the quadrupole coupling and shift parameters can be made on powder specimens at frequencies well below the lowest pure quadrupole frequency. In less detail, we have also studied the halogen resonances in sodium chlorate [$\nu_Q(Cl^{35}) \sim 30$ Mc/sec] and in sodium bromate [$\nu_Q(Br^{81}) \sim 150$ Mc/sec].

As noted by Abragam,[1] the generalization of (1), and hence of (3), to larger half-integral spin values leads to the approximate (first-order) resonance condition, $\nu = (I+\frac{1}{2})\nu_L$, for spin I. However, consideration of the relative transition probabilities shows that in the case of spin $\frac{5}{2}$, for example, the 3γ resonance has only weak intensity, and that, instead, the more intense resonance should be the $|\Delta m| = 3$ transition

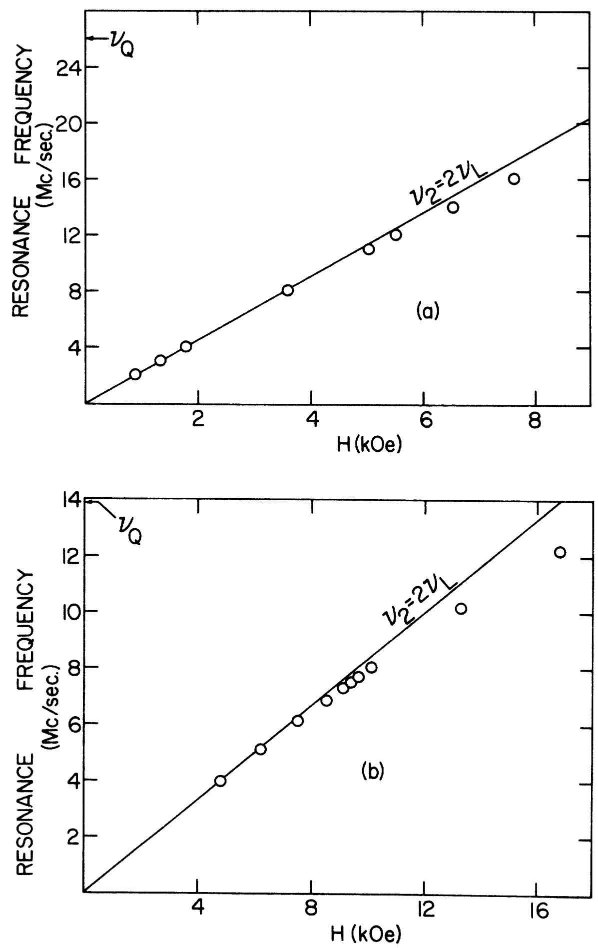

FIG. 2. Frequency-versus-field behavior of the "double Larmor frequency" resonance in two spin-$\frac{3}{2}$ cases: (a) Cu^{65} resonance in Cu_2O, (b) Cl^{35} resonance in K_2ReCl_6. In both cases, the solid straight line is drawn for $\nu_2 = 2\nu_L$.

between the $\pm\frac{3}{2}$ levels (quadrupole states labeling) which occurs at very small effective γ. In the spin-$\frac{3}{2}$ case, the $|\Delta m| = 3$ transition (the 0γ transition of Fig. 1) has the weak intensity.

We have been unable to detect any resonance at the 3γ position for a spin-$\frac{5}{2}$ nucleus experiencing a large quadrupole interaction (e.g., I^{127}) in a powder specimen.

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[1]A. Abragam, The Principles of Nuclear Magnetism (Clarendon Press, Oxford, England, 1961), p. 257.

[2]M. H. Cohen and F. Reif, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

[3]N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[4]S. Kojima, K. Tsukada, A. Shimauchi, and Y. Hinaga, J. Phys. Soc. Japan 9, 795 (1954).

[5]H. Cox and D. Williams, J. Chem. Phys. 32, 633 (1960).

[6]R. Ikeda, D. Nakamura, and M. Kubo, J. Phys. Chem. 69, 2101 (1965).

QUANTUM TRANSITIONS AND LOSS IN MULTIPLY CONNECTED SUPERCONDUCTORS

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This Letter reports on the observation of quantized flux flow across superconducting weak links.[1] This is accomplished by incorporating the weak link into a macroscopic superconducting ring and making use of the quantum behavior of this multiply connected superconductor. The quantized flux flow corresponds to direct transitions between the allowed states of the ring. Within this simple model we offer a criterion for the appearance of a fundamental resistive effect associated with the passage of flux across superconducting elements; this criterion was experimentally verified. Thus we have performed an elementary experiment on the dynamics of the quantized fluxoid which is pertinent to the recent discussions on voltages and resistance in superconductors.[2-5]

The experiment consists of measuring the current and voltage across a superconducting weak link or point contact in an otherwise macroscopic superconducting ring as shown in Fig. 1. The ring was made of niobium, the point contacts were adjustable 000-120 niobium screws,[6] and all experiments were performed at 4.2°K. With the superconducting ring open at point (b), the maximum supercurrent, i_c, of the contact at (a) is measured. Following this the ring is closed at (b) and the voltage across the link is measured as a function of the source current, I, and of maximum supercurrent, i_c.

The multiply connected superconducting states of the ring can be characterized by the quantum condition on the phase integral around the ring,[7] using standard notation,

$$\oint \vec{p}\cdot d\vec{l} = kh, \qquad (1)$$

where $\vec{p} = 2m\vec{v} + 2e\vec{A}$ is the canonical momentum of the coherent electron pairs and k is an integer. Since the bulk portion of the ring is thick compared to the London penetration length, λ, we can always find a path such that $\int m\vec{v}\cdot d\vec{l}$ vanishes in the bulk superconductor. However, the thickness of the link is comparable to or

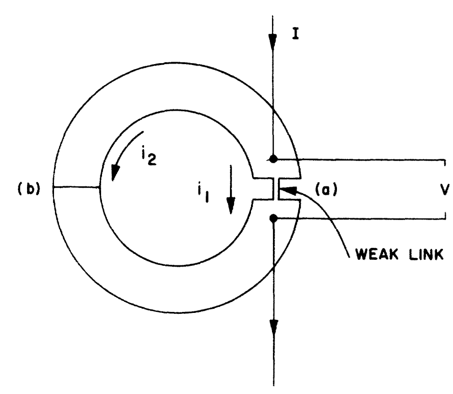

FIG. 1. Schematic of the macroscopic superconducting ring with the weak link. I is the total external current, i_1 the current in the weak link, and i_2 the current in the ring.