Many-Quantum Transitions in a Rotating Reference Frame*

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Many-quantum transitions have been observed in conduction-electron spin resonance where the quantization is along the effective field in the rotating frame. The relative intensities of the higher-order transitions as a function of the applied perturbing field are given. These intensities exhibit the field dependence expected.

IN the years following Redfield's[1] introduction of the concept of spin quantization in the rotating frame there has been a vigorous and fruitful investigation of nuclear spin systems[2,3] resulting in an overwhelming support of this hypothesis. To the authors' knowledge only two reports on electron spin systems has appeared.[4,5] While both of these reports supported the validity of the concept of spin quantization in the rotating frame for electrons, the present work demonstrates that the rotating frame affords an easy way to study higher-order effects that are too weak to observe in ordinary electron spin resonance (ESR).

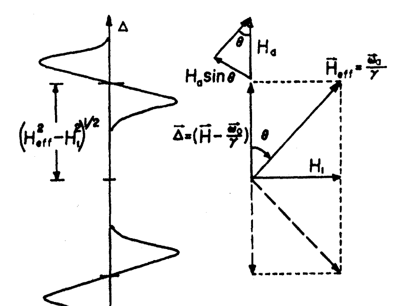

FIG. 1. The positions of the resonances $\hbar\omega_a = \hbar\gamma H_{eff}$ as the H field is swept through the resonance in the lab frame $\hbar\omega_0 = \hbar\gamma H$ ($\Delta = 0$). The spectrometer coil along H will produce only a component ($H_a \sin\theta$) of its perturbing field perpendicular to H_{eff}.

The spin system used was that of the conduction electrons in Li metal in a crystal of LiF which had been neutron irradiated and subsequently annealed at 700°C.[6] The unsaturated ESR resonance line has a width of 350 mG in our experimental arrangement, implying relaxation times of $T_1 \gtrsim T_2 \approx 10^{-6}$ sec. With the field scan of ~5 G/min and modulation frequency of 400 Hz employed, the spins in the rotating frame always fulfilled slow passage conditions. Saturation of the ESR resonance, a necessary condition for Redfield's[1] hypothesis, was ensured by using an Elliott-type 8TFK2 klystron capable of 10-W output at 34 GHz. The maximum H_1 field obtained in the TE_{104} cavity[4] was 0.8 G. The rotating frame magnetization was observed by placing a coil along the steady magnetic field direction just outside the cavity. This is the only direction common to both the lab and rotating frames. The magnetization was detected by using a marginal oscillator[7] operating between 2 and 10 MHz. The field H_a of the marginal oscillator could be varied from 0.5 to 2.0 G.

Figure 1 shows the spectrum one expects in our arrangement for resonance in the rotating frame for a single ESR line (e.g., conduction-electron resonance). One should note that the ordinary ESR resonance would occur at $H_{eff} = H_1$ ($H = \omega_0/\gamma$). Since the component of the magnetization along the steady external field H is always in the same direction whereas the magnetization along H_{eff} changes sign, one observes an absorptive line for H above the ESR resonance and an emissive line below the resonance position.

One of the more interesting properties of the rotating reference frame is that the field of quantization $H_{eff} = (\Delta^2 + H_1^2)^{1/2}$ is of the order of a few gauss. Thus the resonance is carried out in a very small "static" field. This implies that higher-order effects which in ordinary ESR depend on $(H_{local}/H)^2$ and $(H_1/H)^2$ being not too small now depend on $(H_{local}/H_{eff})^2$ and $(H_a/H_{eff})^2$ which in fact can easily be made larger than 1. One would expect therefore to observe higher-order dipolar resonances[8] and many-quantum transitions.[9] Such effects have recently been observed in a nuclear spin system[3] but under less favorable conditions than with the present electron system. This is mainly because the narrow electron-resonance line affords a much higher resolution.

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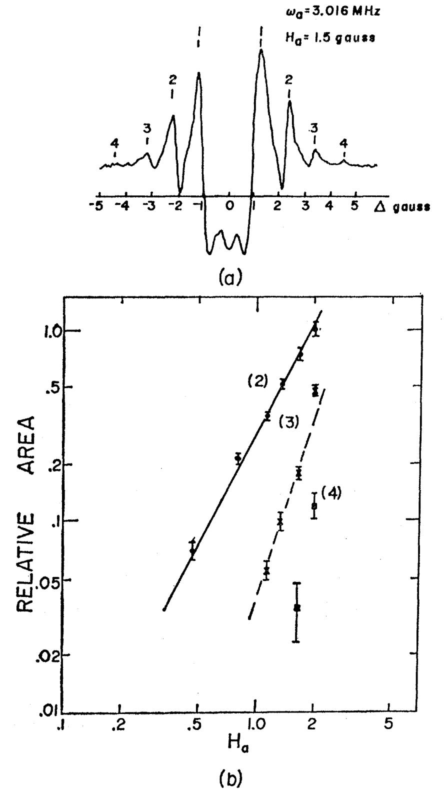

FIG. 2. (a) A typical sweep of the absorption spectrum after lock-in detection. The one-, two-, three-, and four-quantum transitions are noted. The peak around $\Delta=0$ is a nonresonant effect. (b) Plot of the intensities of the many-quantum transitions relative to the single-quantum transition as a function of H_a. The data for the two-quantum transition are proportional to H_a^2. For comparison a dashed line proportional to H_a^4 is drawn through the three-quantum transition data.

A typical sweep with the many-quantum transitions indicated is given in Fig. 2(a). Owing to the fact that H_a has components both parallel and perpendicular to H_{eff}, one expects[9] to observe both even and odd multiple transitions of the perturbing frequency ω_a.

Several such composite spectra, obtained at a given ω_a but varying the intensity of the perturbing field, were analyzed by fitting each trace with normalized line shapes for the various transitions. The line shape used was that of a trace taken with very low H_a where the single transition only is observed as in Fig. 1. The many-quantum transitions had the same linewidth within the experimental error. The relative areas were then calculated and plotted against log H_a as shown in Fig. 2(b). The data of the two-quantum transition are the most reliable. The relative intensity of this transition with respect to the single-quantum transition is proportional to $(H_a/H_{\text{eff}})^2$.

Preliminary results show that the many-quantum transition lines are also shifted as expected[9] but the experimental error at this time does not allow a comparison with theory. The shift is of the order of 0.1 G in 12 kG. Experimental refinements as well as a complete analysis are in progress. [*Note added in proof.* Good agreement between the experimental results and theory have been obtained by using a modified Bloch equation under the assumption that $T_1=T_2=T$ and that the spin system relaxes towards the instantaneous field.]

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