

Dispersion electron spin resonance with the loop-gap resonator

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The loop-gap resonator, a novel microwave lumped-circuit structure, when used as a sample resonator in electron-spin-resonance spectroscopy, permits the direct detection of dispersion signals with greatly decreased demodulation of the FM noise that originates in the microwave oscillator. The improvement arises from two factors: 65 times higher energy density for a given input power and 12 times lower resonator Q compared with a typical cavity resonator. The signal-to-noise ratio for the dispersion signal of DPPH is predicted to be improved by a factor of $12 \times 65 = 780$; experimentally a factor of 700 was realized.

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In ESR spectrometers, an experimental problem has long existed in the detection of the dispersion signal χ' . Dispersion causes change of resonant frequency of the microwave resonator, and a microwave bridge that is adjusted to detect such a change is at the same time maximally sensitive to demodulation of frequency modulation (FM) noise of the microwave oscillator.

A number of experimental approaches have been proposed to overcome this problem. Wilmschurst,¹ citing an earlier paper by Mehlkopf and Smidt,² discusses noise cancellation schemes in which a bridge arrangement is

employed with two matched resonators, one of which contains the sample. Teaney *et al.*,³ Huisjen and Hyde,⁴ and more recently Mailer *et al.*,⁵ describe microwave bimodal cavities in which only magnetic resonance phenomena couple the modes, and otherwise the microwave source is isolated from the receiver. These systems can be made to work well but are difficult to adjust. Other approaches to the problem involve trying to decrease the FM noise itself including: (a) use of two cavity klystrons rather than reflex klystrons (but cost precludes this method); (b) use of high- Q microwave stabilization cav-

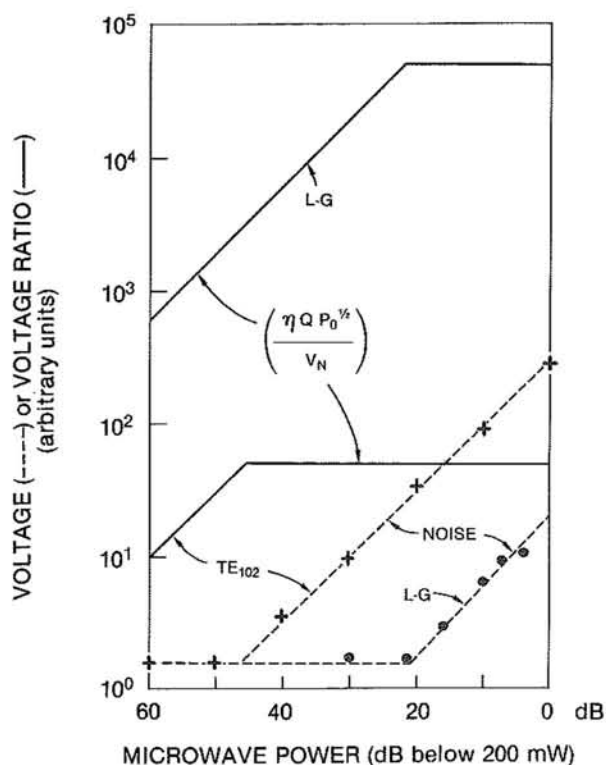


FIG. 1. Dashed lines: noise voltage as a function of incident power when tuned to the dispersion in a normal Varian reference arm type X-band bridge with the AFC off using a Varian E-231 TE₁₀₂ rectangular cavity at 9.5 GHz and a loop-gap (LG) resonator at 8.8 GHz. Solid lines: signal-to-noise ratios for an unsaturated point sample.

ities tightly coupled to the oscillator (but these are narrow band and result in loss of power); (c) harmonic generation from a quartz crystal, and microwave amplification to create a spectrally pure source.

We believe we have found a superior solution to this old problem, and report the results in this note.

We have previously described^{6,7} a novel lumped-circuit microwave resonator, termed a loop-gap resonator. In the X-band version of this resonator used in the present experiment, the microwave magnetic field is concentrated in a cylindrical region or loop of 1 mm diam, 2.5 mm high, with an unloaded Q_0 of about 650. The energy density is about 65 times higher than in a conventional resonant cavity. At the same time, since it is a lumped circuit, the energy associated with the rf electric field tends to reside in the capacitor rather than the loop so that problems of dielectric loss are minimized. We have demonstrated that excellent ESR sensitivity over a wide range of samples can be obtained with this resonator.

There are two important properties of this resonator that make it ideal for direct detection of the dispersion: the relatively low Q and the very high-energy density for a given incident power. For direct detection of dispersion, the automatic frequency control (AFC) is turned off and the microwave reference phase is shifted by 90°. The dispersion will then be detected.

In order to set the reference phase properly, a 70-kHz AFC voltage continues to be applied to the reflector of

the klystron even though the 70-kHz phase-sensitive detector (psd) output is disconnected from the klystron reflector so that the AFC loop is not closed. This psd output is continuously monitored with a voltmeter. When the microwave phase is correctly set to detect dispersion, the voltmeter reading will be maximum.

The cooling water for the klystron in our spectrometer is temperature regulated and the room is air conditioned. Under these conditions, stability of the instrument is adequate. Most of our work thus far has been performed in open-loop configuration (i.e., AFC off). Nevertheless, we are of the opinion that AFC control is desirable for improved long-term stability. Hyde⁸ pointed out that one can lock the resonant frequency of the oscillator and sample resonator and still detect dispersion so long as the AFC has negligible loop-gain at the Zeeman field-modulation frequency. Since long-term stability is all that is required, this condition is not difficult to satisfy. In his patents,^{8,9} several schemes were described including: (a) sampling a portion of the power reflected from the cavity for AFC purposes; (b) a sample-and-hold type AFC with time-modulated shift of the reference phase by 90°; and (c) use of an AFC in which an even rather than odd harmonic of the modulation that is applied to the reflector of the klystron is detected.

Figure 1 (dashed lines) shows a comparison of noise characteristics when detecting the dispersion as a function of incident microwave power for the loop-gap (LG) resonator and a conventional rectangular TE₁₀₂ cavity resonator. (It is noted that microwave voltages are de-

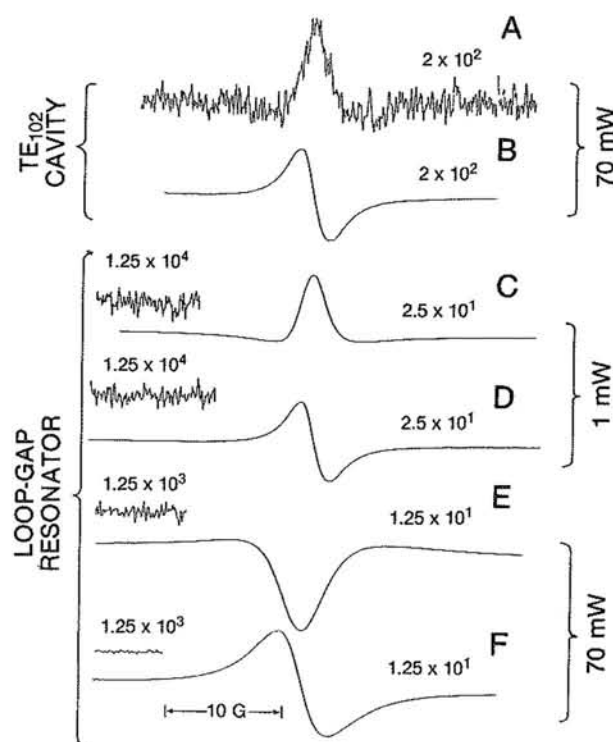


FIG. 2. Comparison of signals from DPPH in the TE₁₀₂ and loop-gap resonators. A and B were at 9.5 GHz and C to F at 8.8 GHz. For all spectra: 0.128-s time constant, 0.1-G field modulation amplitude, room temperature, 40-G scan in 2 min. Spectrometer gains are indicated.

ected in a bridge that employs a microwave reference arm.) Break points are observed for the TE₁₀₂ and loop-gap resonators at 46 and 21 dB attenuation of incident microwave power P_0 , respectively. Below these points, detector crystal noise, which is independent of P_0 , dominates, while above these points demodulation of klystron FM noise, which varies as $P_0^{1/2}$, dominates. One expects the ratio of break-point powers to be given by the square of the ratio of Q 's. We have

$$Q_0(\text{TE}_{102}) = 7900 \pm 400,$$

$$Q_0(\text{LG}) = 650 \pm 50,$$

$$10 \log_{10}[Q_0(\text{TE}_{102})/Q_0(\text{LG})]^2 = 22 \text{ dB} \pm 1 \text{ dB}. \quad [1]$$

This can be compared with the experimental value of (46 - 21) dB = 25 dB, which is fair agreement. The difference could arise from different noise characteristics of the klystron at 9.5 and 8.8 GHz. Above 21, dB the ratio of noise voltages for the two resonators is given by the ratio of Q 's.

Figure 1 (solid lines) shows the relative signal-to-noise ratios for a nonsaturable point sample in the two resonators. Here, the noise was experimentally determined (dashed lines) and the signal was assumed to behave as expected theoretically. At powers below the TE₁₀₂ breakpoint (46 dB), the noise is independent of P_0 , the signal-to-noise ratio varies as $P_0^{1/2}$, and the relative advantage of the loop-gap resonator is 65 times and is determined by the ratio of ηQ products, where η is the filling factor.¹⁰ Above the 46-dB breakpoint, the advantage of the loop-gap resonator increases further because the signal-to-noise ratio with the TE₁₀₂ cavity is independent of P_0 , while the signal-to-noise ratio with the loop-gap resonator varies as $P_0^{1/2}$. The advantage plateaus at a factor of 1000 times improvement at 21 dB attenuation of the incident microwave power. A factor of 780, which is the product of the ratio of Q 's and the ratio of energy densities, is predicted theoretically. It is interesting to note, when directly detecting dispersion at highest incident powers, that both the signal and the noise vary linearly with Q , and in the absence of microwave power saturation the signal-to-noise ratio depends only on the filling factor.

Figure 2 illustrates these ideas for a small speck of DPPH (2,2-diphenyl-1-picrylhydrazyl) probably containing several crystallites. Figures 2A to D show no microwave power saturation, while some broadening and the onset of saturation behavior is evident in Figs. 2 E and F. The signal amplitude comparing A, B with C, D gives an ηQ ratio for the two resonators of

$$\left(\frac{\text{signal (LG)}}{\text{signal (TE}_{102})} \right) \left(\frac{P_0(\text{TE}_{102})}{P_0(\text{LG})} \right)^{1/2} \approx 60, \quad [2]$$

which equals the predicted value of 65 when the Boltzmann factor for the two microwave frequencies is taken into account. The noise, comparing A with E at 70 mW, where source noise dominates for both resonators, is about 12 times higher for the TE₁₀₂ resonator, a value that is very close to the ratio of Q 's. The experimental

signal-to-noise ratio for the dispersion at 70 mW is 200 times better for the loop-gap resonator. If no saturation occurred, one can see by comparing the signal intensities of A and C and multiplying by $70^{1/2}$ that the improvement would be 700 times. This is in satisfactory agreement with the predicted theoretical factor of 780 and the factor of 1000 obtained from analysis of noise characteristics, taking into account inherent difficulties in noise measurements.

As a further illustration, spectra from a nitrogen-centered defect in a single crystal of diamond are shown in Fig. 3. The absorption signal is just discernible under optimum conditions in a cavity resonator A, and is about 75 times more intense in the loop-gap resonator B. The absorption and dispersion signals saturate differently. The saturation behavior of the absorption signal behaves as predicted by Portis¹¹ for an inhomogeneous line, the signal amplitude being nearly independent of power between 2 μ W and 1 mW. The dispersion signal Fig. 3C, D, however, increases in amplitude by a factor of 10 in this range of powers and shows indications of rapid-passage effects.^{12,13} These effects are of course a complication, but nevertheless this observed difference in signal-to-noise ratios between A and D of a factor of 500 for an easily saturated signal can be useful.

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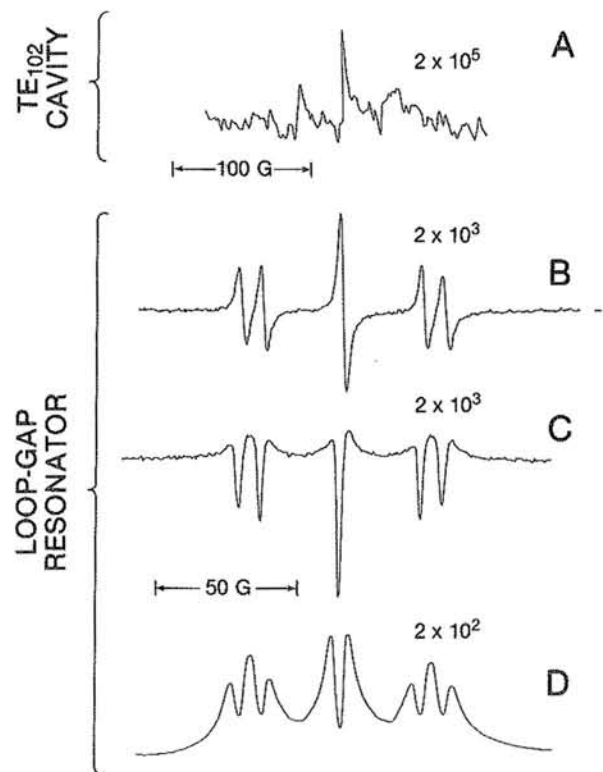


FIG. 3. Comparison of signals from a single-crystal synthetic diamond in the TE₁₀₂ and loop-gap resonators. For all spectra: room temperature, 2-G field modulation. Spectrometer gains are indicated. A. 1 mW, 9.3 GHz, 1-s time constant. B, C. 2 μ W, 8.81 GHz, 0.25-s time constant. D. 1 mW, 8.81 GHz, 0.25-s time constant.