

VERY HIGH FIELD EPR SPECTROSCOPY

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I- Introduction

Since the very beginning of high resolution NMR spectroscopy, in order to make easier the spectral analysis and to improve the sensitivity, spectrometers have been built to operate at magnetic fields as high as possible. Because EPR spectroscopy is much more sensitive than NMR spectroscopy and because the EPR spectra are usually easier to analyze the situation in EPR spectroscopy is completely different. The great majority of EPR spectrometers are working at $B_0 \sim 0.34$ T (X band) or $B_0 \sim 1.25$ T (Q band).

There has been a few attempts to record EPR spectra at high magnetic fields. Two spectrometers working at 5.3 T ($\lambda=2$ mm, $\nu=148$ GHz) [1] and at 3.4 T ($\lambda=3.2$ mm, $\nu=94$ GHz) [2] respectively, which uses microwave technology have been built up. More recently a spectrometer working at 9 T ($\lambda=1.2$ mm, $\nu=250$ GHz), using free space propagation via lenses to guide the far infrared (FIR) radiation emitted by a Gunn diode has been described [3]. These

spectrometers have been mainly used for the study of free radicals in solution. For the investigations of impurities in semiconductors, Wagner et al. [4] built an EPR absorption spectrometer, operating at 9 T. We report here of a FIR absorption EPR spectrometer, which may work up to 19 T.

II- Experimental

In this section are described the three main parts of the spectrometer namely the radiation source, the detector and the magnet. As our goal was to build a spectrometer tunable over a frequency range as broad as possible, an optically pumped FIR laser was chosen as excitation source. Such a laser is made of three main parts: a tunable CO_2 pump laser, a FIR resonator and the coupling optics between the two lasers (Fig 1).

The pump is PL4 Edimburg Instruments CO_2 laser. The FIR resonator is home made, optimized for the wave-

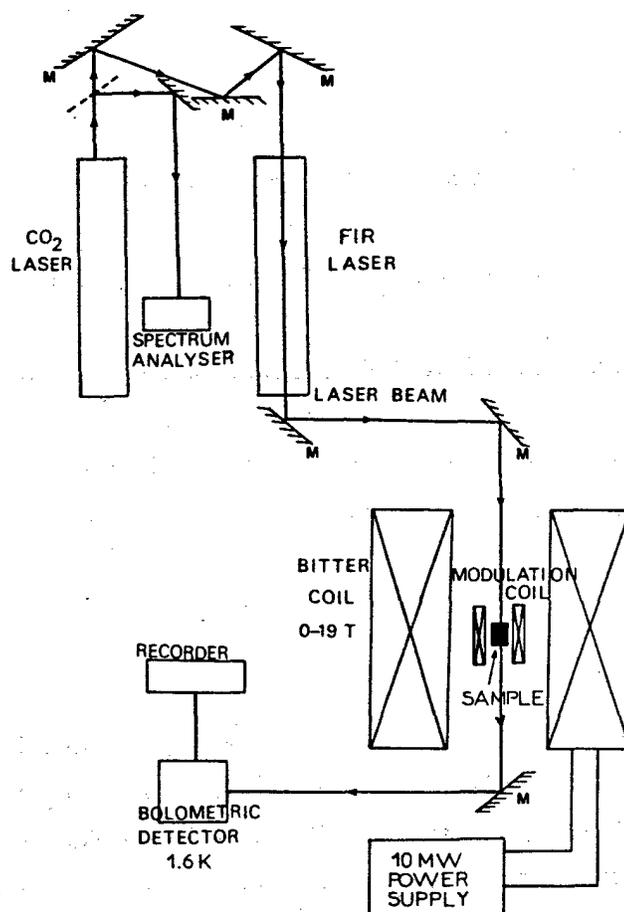


Figure 1 Schematic diagram of the EPR spectrometer

lengths of interest. This resonator is made of an invar cavity consisting of two flat mirrors one fixed, one moveable and a hollow metallic waveguide [5]. The laser gases are continuously flowed through the cavity. The FIR output stability is greatly improved, using in the coupling optics the passive isolator described by Mansfield et al. [6].

The wavelengths of the commonly used laser lines are listed in the table.

To cover the 0.5 mm to 2 mm wavelength range with an optimum signal to noise ratio we use a composite bolometer detector cooled at 1.6 K. This de-

λ (μm)	ν (GHz)	B(T)
570.57	525.43	18.75
699.42	428.63	15.30
1020	293.9	10.49
1223.67	244.99	8.74
1899.89	157.79	5.63

Table Wavelengths and frequencies of the commonly used laser lines together with the corresponding magnetic field for the free electron g factor ($g \sim 2.00$), detector has already been described in detail [5].

The magnetic field is provided by a Bitter magnet designed to produce a magnetic field up to 19 T with a relative

homogeneity of $3 \cdot 10^{-5}$ over a 1 cm diameter sphere.

In this high magnetic field spectrometer we do not use a resonant cavity. For samples with high spin concentrations the EPR signal is measured directly through changes in the transmission of the sample. For low spin concentrations, in order to increase the sensitivity of the system, the magnetic field modulated transmission is recorded, thus observing the derivative of the transmission (the meaning of high or low spin concentrations will be explained in the next section).

We worked in either the Faraday configuration (the electromagnetic wa-

vevector k of the exciting radiation is parallel to the magnetic field B_0) or in the Voigt configuration (k is perpendicular to B_0). With a laser which delivers lines at fixed wavelength we record the spectra by sweeping the magnetic field.

III- Results and discussion

The sensitivity and resolution of the spectrometer were tested using 125 mm^3 cubed samples of n-type Silicon doped with Phosphorus (85 %) and Arsenic (15 %) (Fig 2), the carrier concentration being of $5 \cdot 10^{15} \text{ cm}^{-3}$. At 4.2 K, $5 \cdot 10^{13}$ spins/gauss are detected. A

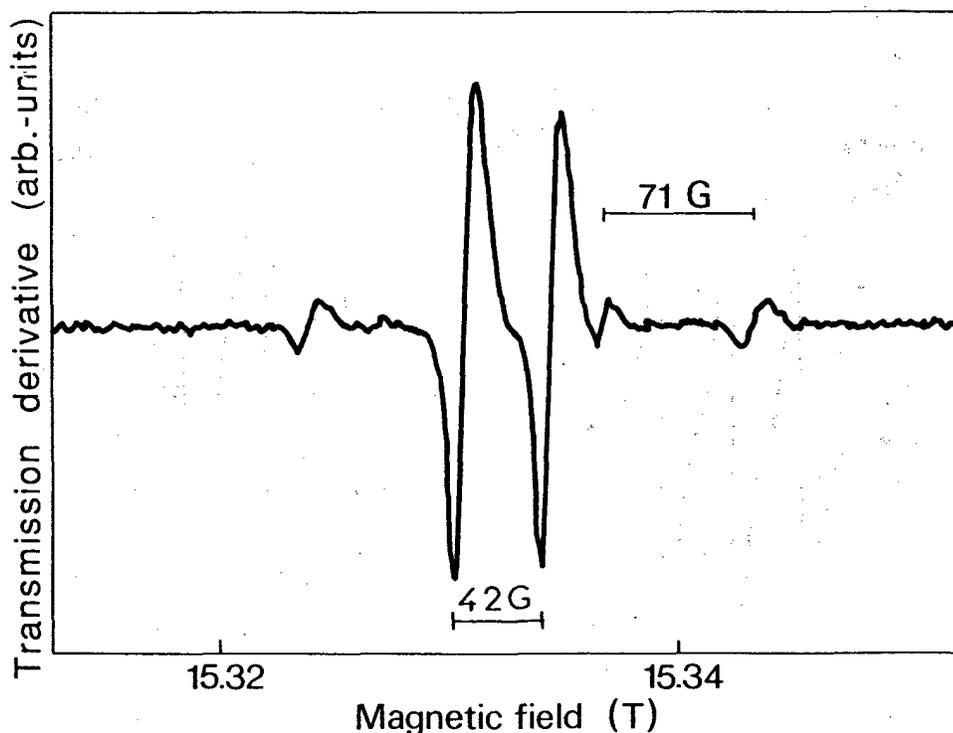


Figure 2 EPR spectrum of n-type Si. $\lambda = 699 \mu\text{m}$, $T = 4.2 \text{ K}$

spectrum is shown in Fig 2. The two stronger lines correspond to the spin 1/2 Phosphorus coupling ($a=42$ gauss), three of the four lines due to the spin 3/2 Arsenic ($a=71$ gauss) are observed. The Phosphorus resonances have a half-width of 6 gauss at a field of 15 T, which corresponds to a resolution $\Delta B/B \sim 4 \cdot 10^{-5}$.

The study of n-type Silicon illustrates two of the major advantages of the present technique over the low field EPR spectroscopy. Firstly, owing to the large decrease of the spin-lattice relaxation time of our semiconductor samples with the applied magnetic field, spectra have been recorded down

to 1.6 K, whereas with low field spectrometers absorption measurements can only be obtained at $T > 10$ K. Secondly, the resonance lines of electrons with slightly different g factors is measured. The difference in the g factors of P and As in n-type Silicon is:

$$g_P - g_{As} = (15 \pm 2) \cdot 10^{-5}.$$

The spectrometer has been used to study doped semiconductors such as GaP:S and the results [7] illustrate another potentiality of this technique, namely the possibility to observe simultaneously electric dipolar transitions and magnetic dipolar transitions.

In order to assess the performances of this spectrometer for liquid state

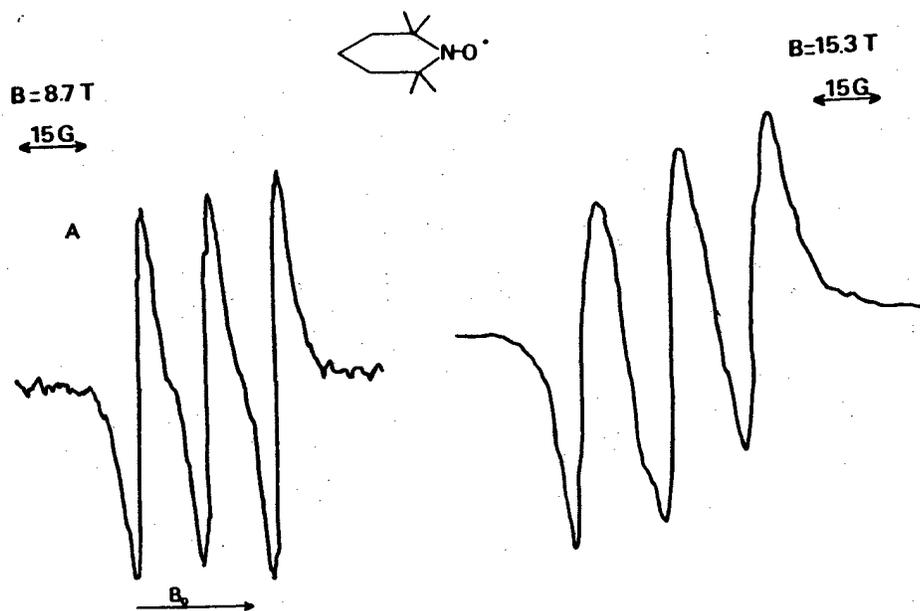


Figure 3 EPR spectra of Tempo in Toluene at 8.75 T and with a dilution of 10^{-3} M (left), at 15.30 T and with a dilution of 10^{-2} M (right)

studies, we have first recorded spectra of a stable and well-known free radical Tempo (2,2,6,6-tetramethylpiperidin-1-oxyl), dissolved in perdeuterated Toluene [8]. With a dilution of 10^{-3} M, which corresponds to 10^{17} spins, one observes the expected 1:1:1 triplet due to the hyperfine coupling ($a_N \sim 15$ gauss) of the free electron with the spin 1 Nitrogen nucleus (Fig 3).

The spectrometer we built makes a link between conventional EPR and FIR spectroscopy. Its potential utility may be considered in different areas: study of relaxation times as a function of magnetic field; detection of new species of close g values; study of weakly anisotropic g tensors; spectral density function analysis in relation with molecular dynamic studies; measurements of large hyperfine nuclear-electron spin coupling; possibility to record spectra in which a large zero-field splitting prevents to detect transitions with conventional spectrometers; study of dynamical processes using the spin labelling technique.

IV- References

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