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PHOTOACOUSTIC DETECTION OF EPR IN SOLIDS

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The photoacoustic effect (PAE) has become an efficient tool to investigate processes which involve the generation of heat. In the past the PAE has found diverse applications in optical spectroscopy and ac calorimetry[1,2]. The method has now been applied to the detection of absorption in the microwave region, electron paramagnetic resonance (EPR)[3,4,5]. Although the calorimetric determination of EPR is already a well studied technique[6,7] its combination with the acoustic response of a transducer gas may deliver some new information.

In this contribution we report on PA detected EPR experiments performed on polycrystalline samples of DPPH and $CuSO_4 5H_2O$ in the temperature range between 77K and 300K.

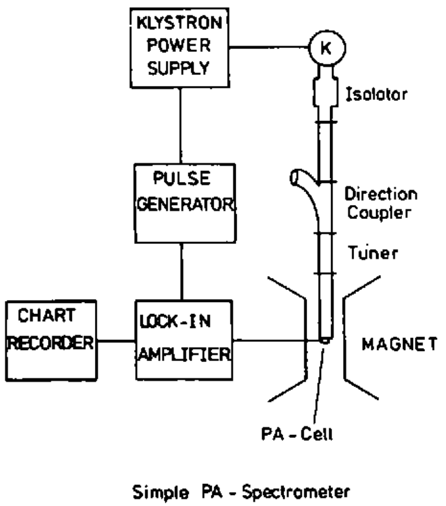

FIGURE 1: Block diagram of the microwave rig used for detecting the PA signal.

The experimental apparatus in its basic form is shown in figure 1. The microwave power is intensely modulated or chopped at a modulation frequency by applying square pulses to the Klystron reflector. The sample to be studied is placed in an acoustically sealed cell containing a gas and a sensitive microphone and is positioned in the shortened end of the waveguide between the poles of an electromagnet.

Figure 2 shows the photoacoustic signal for Diphenyl picryl hydrazyl (DPPH), a

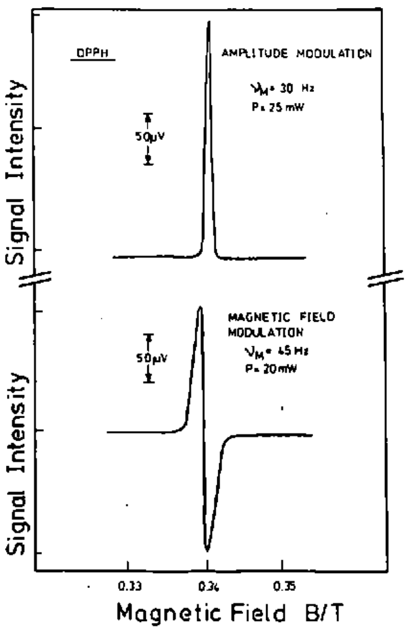

FIGURE 2: Typical experimental spectra of the photoacoustic detection of EPR in DPPH at room temperature.

stable crystalline free radical, used as a marker in conventional EPR measurements. In the top trace of the figure is shown the signal recorded from amplitude modulation. In the bottom, the derivative curve, obtained with field modulation. The g-values and linewidth observed agree well with those obtained by conventional EPR. There is no doubt as to the supercavity of the conventional EPR method with respect to sensitivity and signal-to-noise ratio. The PA detection is of the order of 10^3 to 10^4 less sensitivity particularly for samples such as DPPH, which have a long spin-lattice relaxation time, T_1. This unfavourable condition of PA EPR as compared with conventional EPR alters considerably in the case of broad resonance lines (short relaxation times T_1) and at low temperature. Figure 3 shows the dependence of the PA EPR spectrum as a function of temperature for $CuSO_4 5H_2O$ in powder form. With

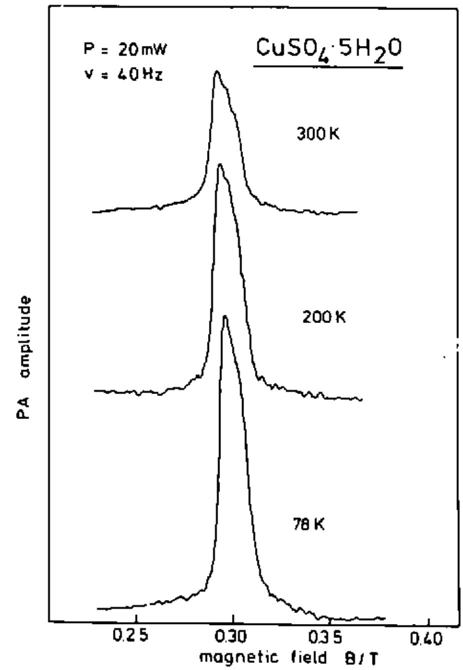

FIGURE 3: Temperature dependence of PA EPR spectra for Cu^{2+} in $CuSO_4 5H_2O$ powder.

decreasing temperature the intensity of the signal becomes considerably enhanced due to two effects: (a) the heat capacity of the solid decreases rapidly ($\sim T^3$) at temperatures below the Debye temperature θ, (b) the pressure response of the surrounding gas medium varies as T^{-1}.

Another important feature of the PA signal is its dependence on modulation frequency ν_m. This is shown in figure 4. The amplitude of the photoacoustic signal increases with decreasing modulation frequency. This does not mean that the signal-to-noise ratio is improved at lower modulation frequencies as the noise appears to be of 1/f in character. For an optically transparent, absorbing or opaque solid sample, in the so-called thermally thick case (where the thermal diffusion length of the sample U_s is less than the optical penetration length α^{-1}) the Rosencwaig-Gersho theory[8] predicts that the PA signal intensity will vary as $\nu^{-3/2}$, in the high frequency limit. The results shown in figure 4 are in excellent agreement with the RG theory.

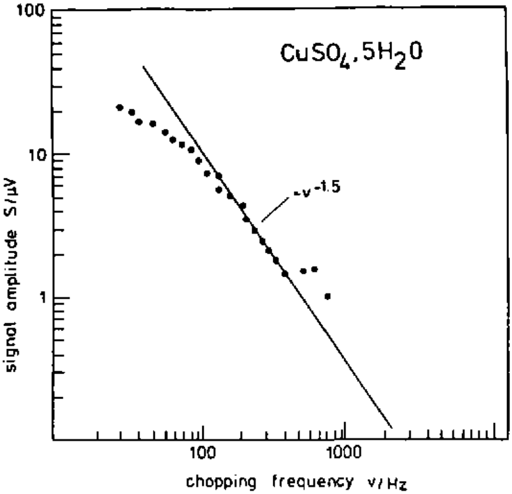

FIGURE 4: Dependence of the signal strength on amplitude modulation frequency for $CuSO_4 5H_2O$ in powder form.

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