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Paramagnetic Resonance Spectrometry at Zero Magnetic Field

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Abstract. The need for direct measurements of paramagnetic resonance absorption spectra in zero magnetic field is discussed. Two spectrometers have been built which together cover the range of 8 to 18 Gc/s; with one of these a spectrum is recorded over a range of nearly 6 Gc/s in a time of two minutes with a sensitivity sufficient to detect about 10^{17} Fe^{3+} ions at 80°K. Polycrystalline samples may be used, and examples are shown of the spectra of a dilute ferric chelate compound. A technique is described for obtaining the absorption line shape free from the effects of the associated anomalous dispersion.

§ 1. INTRODUCTION

THE ultimate aim of paramagnetic resonance absorption studies is to determine completely the behaviour of the energy levels of paramagnetic ions or molecules as a function of magnetic field. In conventional paramagnetic resonance experiments the sample under investigation is subjected to fixed frequency microwave radiation and, in effect, the absorption coefficient is plotted as a spectrum against applied magnetic field up to some 10 000 gauss. Absorption lines occur at the fields where two energy levels of the paramagnetic ions are separated by one microwave quantum, and if the ground energy level in zero field is multiple, with splittings within a few cm^{-1}, the spectrum is multiple with a structure dependent on the inclination of the field to the crystal axes. Because of this anisotropy the maximum information is obtainable only with monocrystalline samples, polycrystals giving a spectrum which is in general diffuse and structureless. The choice of this approach—varying field at fixed frequency—instead of the reverse, was dictated partly by the early concentration of microwave development in a few narrow frequency bands, and partly by the necessity to use high Q cavity resonator techniques to increase sensitivity and so offset the small size of most single crystal samples.

To interpret the results of such experiments a theoretical model is needed: this has been provided by the spin-Hamiltonian of Pryce (1950) and Abragam and Pryce (1951). This model has been highly successful in interpreting many different spectra, but it should be noted that these have mostly been measured under conditions such that the energy equivalent of the steady magnetic field is much greater than the zero-field energy splittings. In other words, the spin-Hamiltonian has largely been tested only at relatively high magnetic fields, and hardly any measurements are available for the opposite case of zero field.

As far as we know, the only substance which has been carefully studied both at relatively high fields and also near zero field is gadolinium ethylsulphate. For this material Bleaney, Scovil and Trenam (1954) found a discrepancy of 90 Mc/s

or 7%—many times the experimental error—between one of the measured zero-field splitting frequencies and that predicted from the high field measurements. This discrepancy has not been explained.   Evidently the theory of paramagnetism in crystals is in need of refinement.   A first step has been taken recently by Koster and Statz (1959), who have produced, by completely general group-theoretical arguments, a secular matrix which contains more elements than that of the spin-Hamiltonian.

Measurements at and near zero field are not only necessary for the further development of theory, but are important, too, for the design of zero-field masers (Bogle and Symmons 1959).   The development of wide-band microwave generators and ancillary equipment has now made such measurements possible, and we have therefore begun the construction of a series of wide-band spectrometers for use at zero field, of which two, covering the range 7·8 to 18·0 Gc/s, are described below.

§ 2. PRINCIPLES OF THE METHOD

In the absence of an applied magnetic field the absorption frequency of a paramagnetic crystal is, of course, independent of its orientation, which can only affect the intensity of absorption.   Samples may therefore be studied in polycrystalline form, and their absorption intensity may be shown to be substantially the same as for favourably oriented material.   Thus a broad-band spectrometer may be constructed simply by connecting a microwave generator to a detector through a piece of waveguide containing a polycrystalline sample, the relatively large size of which partly compensates for the sensitivity lost by giving up the conventional cavity technique.

The fractional absorption of power in a conveniently sized sample of dilute paramagnetic material is only of the order of 0·1% at liquid air temperature. This is much smaller than the changes of transmitted power, over a paramagnetic line width, caused by imperfections of the waveguide system and the frequency dependence of the microwave generator power, so that some method of modulating the intensity, or frequency, of the absorption must be used.   We have used magnetic modulation in almost the same way as the well-known Stark modulation is used in the microwave spectroscopy of gases.   The modulation consists of a field of 80 gauss which is effectively switched on and off 3000 times a second. For the sake of brevity we shall limit our discussion to the case of ions which have doublet levels in zero field (e.g. Fe^{3+}, Gd^{3+}).   When a magnetic field is applied the levels split and each absorption line of a single ion splits into four separate components with frequency separations (of the order of $g\beta B/h$) which depend on the orientation of the crystal axes relative to the modulating field.   For a randomly oriented sample the absorption profile is a smooth curve typified by the dotted line of Fig. 1 (a), spread over a range of about $g\beta B/h$ above and below the zero-field frequency ν_0.   The actual shape of the curve depends on the type of transition considered and need not be symmetrical about ν_0, but these details will be ignored for the present; the essential feature is that the absorption line is broadened and weakened.   In Fig. 1 (b) we show the algebraic difference between the two curves of Fig. 1 (a).   It is clear that it may be obtained experimentally by scanning the microwave frequency, applying modulation to the sample and recording phase-sensitively the resulting modulation of transmitted power.   Fig. 2 shows an actual chart record so obtained.

therefore expect that if Marriott's calculations were extended to include $l > 0$ contributions the close coupling exchange approximation would be in even closer agreement with experiment than the present calculation. Indeed, preliminary calculations indicate this to be the case.

§ 4. Scattering of Positrons

Since the positron and the atomic electron are distinguishable, then the problem of using correctly symmetrized wave functions does not arise. However, the possibility of the formation of positronium in these collisions does introduce into the problem an added complication somewhat like exchange effects in the electron scattering problem. That is, including real or virtual positronium formation transforms the problem from solving ordinary differential equations to solving integro-differential equations. The effect of positronium formation has been neglected in this work.

In table 5, we present the elastic scattering cross sections as calculated in the three approximations.

Table 5. Elastic Cross Sections for Positrons

$k_0 a_0$		1s–1s	2s–2s		3s–3s	
	a	0 759(3, 4)	31 45(3),	31 94(6)	196 96(3),	232·81(7)
	b	0 689(3, 4)	31 42(3);	31 87(4)		
1 0	c	0 750(3)			196·87(3)	
	d		27 43(3)		194·08(3)	
	e	0 689(3)	27 12(3)		194 01(3)	
	a		21 72(4);	22·5 (10)	85·64(4),	139 16(8)
	b	0 586(4, 5)	21 65(4);	22 54(5)		
1 2	c	0 640(4)			85·78(4)	
	d		18 58(4)		81 80(4)	
	e	0 586(6)	18 48(4);	19 07(6)	82·04(4),	121 03(6)
	a		13 12(4),	15 13(12)	36 14(4),	78 53(9)
	b	0 475(5, 6)	13 06(4);	14 75(6)		
1 5	c	0 513(5)			36 05(4),	47 77(5)
	d		11 85(4)		34 71(4)	
	e	0·473(5)	11 77(4);	12 78(5)	34 75(4),	46 70(5)
	a		7 36(5),	8 96(13)	19 38(5),	40 39(11)
	b	0 349(7)	7 33(5);	8 45(7)	18 13(5),	26 0 (7)
2 0	c	0 366(7)				
	d		7 29(5)		19 15(5)	
	e	0 345(6)	6 94(5),	7 58(6)	18 99(5);	23 61(6)

Once again it is noted that including more s-states does not affect the cross sections, which supports the conclusions of Massey and Moussa (1958) that distortive effects are unimportant but conflicts sharply with Spruch and Rosenberg (1960) and Moussa (1959). Because of this disagreement, numerical solutions of the positron's integro-differential equations are needed.

§ 3. Description of the Spectrometers

Two spectrometers have been built, one covering the frequency range known as J-band (12·4–18·0 Gc/s) and the other 7·8–12·4 Gc/s, which is slightly more than X-band. Both can be operated at liquid air or liquid helium temperatures.
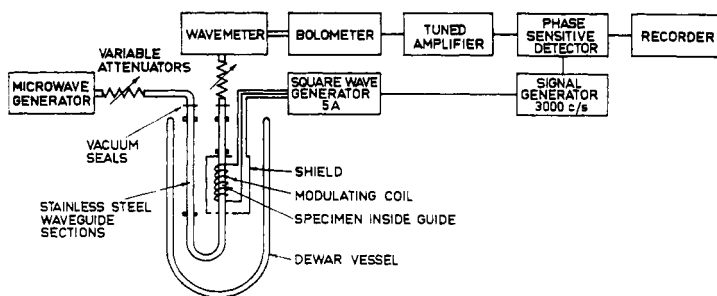

Fig. 4. The J(K$_u$) band transmission system.

The J-band spectrometer is shown schematically in Fig. 4. The microwave generator is a Hewlett–Packard sweep oscillator, model 687A, which contains a Huggins HO–4B backward-wave oscillator. The frequency may be swept electronically at various rates over the entire J-band, the frequency varying linearly (within 6%) with time. The slowest rate, at which the band is swept in 130 seconds, is well suited to our purpose. The transmitted power is detected by a broad-band bolometer and mounting (Narda type 604 and 529 respectively). The modulating coil is wound around the waveguide with spacers which allow the liquid coolant to circulate between the two and so prevent heat from the coil affecting the temperature of the waveguide and sample. The coil produces 16 gauss per ampere, and is supplied with a 5 A square-wave current from a transistor circuit. The waveguide is slotted to prevent eddy currents. Unwanted pick-up from the coil is reduced by a shield pierced to allow free convection of the coolant within it. The bolometer amplifier is a Sanders transistorized voltage standing wave ratio amplifier, which can be operated selectively at 1000 or 3000 c/s with a bandwidth of about 200 c/s. The various charts of J-band absorption spectra which are shown in this paper were each taken in a time of 130 seconds. We believe that their frequency range—nearly 6 Gc/s—exceeds that of any microwave spectrum previously recorded in a single run.

The generator for the X-band spectrometer (Fig. 5) is a klystron (Varian X–13) which must be tuned mechanically. At present, spectra are measured point by point. The reflection system used here has the advantage of compactness, but the disadvantage of uncertainty whether all the power reaching the detector has traversed the paramagnetic sample. We now consider a transmission system to be preferable. In Fig. 6 we show a plot of the absorption spectrum of Fe^{3+} in $Al[(CH_3CO)_2CH]_3$ in the X-band at 90°K, and in Fig. 3 a detailed plot of the 9·3 Gc/s line at 80°K for modulation both from 0 to 100 and from 100 to 200 gauss. These results were taken without a phase-sensitive detector. Since the 100 to 200 gauss modulation curve in Fig. 3 is so flat, the 0 to 100 gauss modulation curve gives nearly the true line shape. The whole width at half intensity is 80 ± 5 Mc/s. We believe that this is the first determination of a paramagnetic resonance line shape at zero field.

A paper dealing in detail with these results is in preparation, and will appear later.

The major experimental problem which we have encountered is the avoidance of what we term 'interferometer fringes'. By this we mean the sharp wiggles on the chart of Fig. 7. These fringes only occur near absorption lines. We
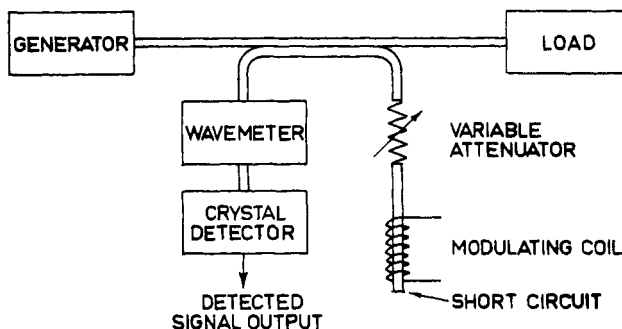
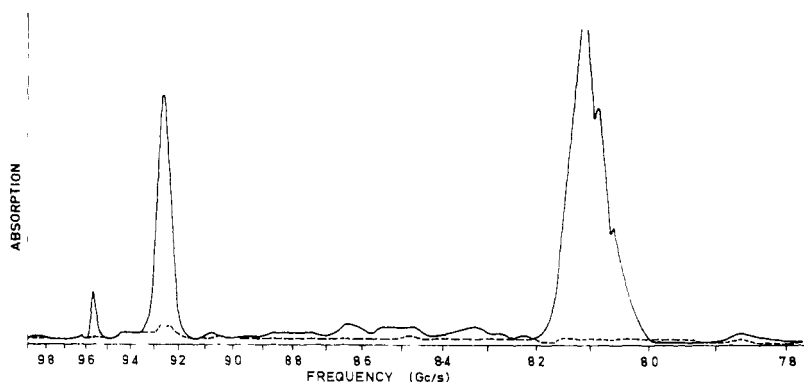Fig. 5. The X-band reflection system.

Fig. 6. The absorption spectrum of (Al, Fe) acetylacetonate at 90°K, between 8 and 10 Gc/s. The peak at 9·56 Gc/s is an ' interferometer fringe ' (see text); other fringes are also discernible.
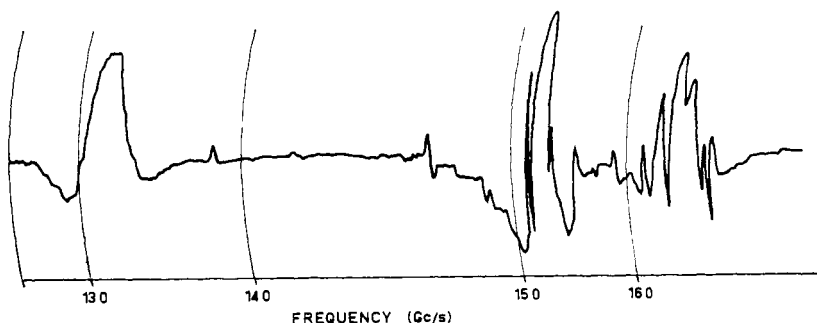
Fig. 7. The absorption spectrum of (Al, Fe) acetylacetonate at 80°K showing undamped ' interferometer fringes '. The reversed scale results from a different method of sweeping frequency.

have not worked out a quantitative theory of the fringes, but think they may be understood qualitatively in the following way: owing to waveguide reflections produced at the external attenuators, the vacuum seals, the waveguide bends and the sample itself, some length or lengths of the waveguide must act like an interferometer in that the transmission shows peaks at a succession of frequencies which correspond to orders of interference.   If the 'interferometer' includes the sample, its effective length is perturbed when the frequency approaches a paramagnetic absorption line because of the associated anomalous dispersion. However, when the modulation field is switched on the anomalous dispersion is much reduced, and so the transmission peaks of the interferometer are shifted in frequency.   Proceeding in this way one can understand the presence of fringes on the chart, and their shapes, and the fact that they are reversed after crossing the absorption line.

The remedy for fringes is to introduce some microwave attenuation at the sample, which can be done by painting parts of the sample-holder with a suspension of colloidal graphite in water ('aquadag'). This damps any waveguide resonances enclosing the sample, and the asssociated transmission peaks or dips are broadened and weakened so that they are much less sensitive to modulation. An attenuation of 3 to 6 dB is generally sufficient.   The improvement may be seen by comparing Figs 2 and 7.

It is perhaps hardly necessary to mention that ferromagnetic materials must be scrupulously kept out of the sample space.   A sliver of steel wool almost too small to be seen with the naked eye produced effects which were much larger than the absorptions shown in Figs 2 and 7.   We have found that 'non-magnetic' stainless steel (type 18/8 F.S.L.) is weakly ferromagnetic at low temperatures, and that if this is used for the waveguide inside the modulating coil similar spurious signals occur.

§ 4. Sensitivity

In the case of the electronically swept J-band spectrometer the choice of the modulation frequency of 3000 c/s, which is unusually high for bolometer detection, is made desirable by the noise characteristics of the backward wave oscillator.   The noise power per cycle per second of bandwidth is 55 and 61 dB below the carrier level at 1000 and 3000 c/s respectively.

The minimum number of Fe^{3+} ions which can be detected at $80°K$ is of the order of 10^{17}.   The sensitivity of the present equipment is limited almost equally by the backward wave oscillator noise and the transistor amplifier noise.

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