ANALYSIS OF SPIN FLIP SATELLITES IN THE SINGLE CRYSTAL EPR SPECTRA

OF ^{63}Cu DOPED (n-Bu$_4$N)$_2$Pt(dtsq)$_2$

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INTRODUCTION

Weak satellites sometimes observed in the EPR spectra have been interpreted as due to concurrent spin flip of an electron and a nucleus close to the paramagnetic centre [1-2]. The intensity ratio between the satellite and the main line for a S = 1/2, I = 1/2 system is given by [1]

$$\frac{I_{sat}}{I_{main}} = \frac{9}{8} \sum_{j=1}^{n} \frac{g^2\beta^2\sin^2\theta_{ij}\ \cos^2\theta_{ij}}{B^2 r_{ij}^6} \quad ...(1)$$

where r_{ij} is the distance between the i-th electron and the j-th nucleus, θ_{ij} is the angle between r_{ij} and the applied magnetic field B, and n is the number of nuclei interacting with the unpaired electron. Bowman et. al. [3] have derived an expression for ΔE, the separation of the spin flip satellite from the main line in energy units.

$$(\Delta E)^2 = (g_n\beta_n B)^2 + (3/4 g\beta g_n\beta_n/r^3)^2 \quad ...(2)$$

From the above equation it is possible to evaluate $r_{\Delta E}$, the average distance to all of the nearest nuclei interacting with the unpaired spin. Thus by combining equations (1) and (2) it is possible to determine the number of flipping nuclei involved in the spin flip transition, by finding the n that makes r_{ij} comparable to $r_{\Delta E}$. Although spin flip satellites have been observed in other metal dithiolenes [4-6], a detailed analysis

has not been carried out. We report here the analysis of spin flip satellites in the single crystal EPR spectra of 1% ^{63}Cu doped (n-Bu$_4$N)$_2$Pt(dtsq)$_2$ where dtsq refers to the dithiosquarate ligand - 1,2,dimercaptocyclobutenedione.

EXPERIMENTAL

Single crystals of (n-Bu$_4$N)$_2$ Pt(dtsq)$_2$ doped with 1% ^{63}Cu, were grown by slow evaporation of a saturated solution of (n-Bu$_4$N)$_2$Pt(dtsq)$_2$ containing 1% of (n-Bu$_4$N)$_2$ ^{63}Cu(dtsq)$_2$ in acetone. Low temperature EPR spectra were recorded on E4/E112 spectrometers coupled with a CTI cryodyne cryocooler/Varian liquid nitrogen cryostat, operating at X-band frequency.

RESULTS AND DISCUSSION

The X-band EPR spectra of 1% ^{63}Cu doped (n-Bu$_4$N)$_2$Pt(dtsq)$_2$ show satellites on either side of the four hyperfine lines arising from ^{63}Cu nucleus. These satellites have been attributed to spin flip transition because of the following reasons : (i) the separation of the satellite from the main line for the M_I = 3/2 line at B = 0.3214T when the magnetic field is parallel to the c* axis is 0.45mT corresponding to 13.07MHz in frequency units, and this value compares well with the theoretically predicted proton NMR frequency of 13.68MHz at this field. Thus

the nucleus undergoing simultaneous spin flip is a proton; (ii) the main line gets easily saturated at higher powers while it is difficult to saturate the satellites. This saturation behaviour which is characteristic of the spin flip satellites, is illustrated in fig.(1), showing the EPR spectra of the system at 69K at low and high microwave powers, when B is parallel to b^*-axis; (iii) intensity of the satellites show an angle and field dependence consistent with that expected by eq.(1). The identification of the proton involved in the spin flip transition was not possible by a selective deuteration of the suspected hydrogen. Instead the information was obtained from crystal structure studies [7]. The hydrogen
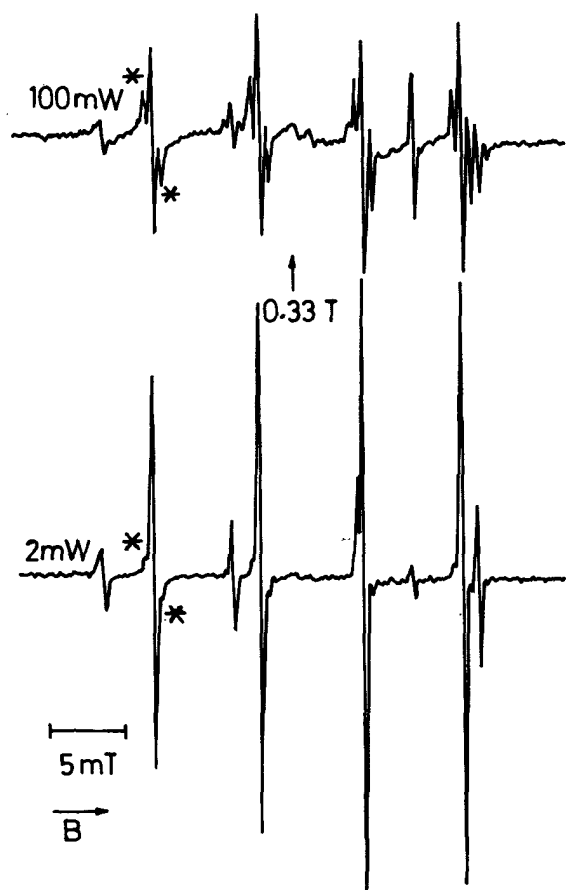

Fig.1 ESR spectrum of ^{63}Cu/Pt dtsq^{2-} B∥ b*-axis at 69 K.

closest to the metal centre was identified as the one from a methylene group which is attached to the nitrogen of the tetrabutyl ammonium cation. This hydrogen was taken to be the one involved in the spin flip. From crystal structure analysis the distance between this hydrogen and the paramagnetic metal centre was found to be 3.04 Å

In order to calculate r from eq.(1) EPR spectra were recorded at various microwave powers at room temperature with B parallel to the c^* axis of the crystal. With the aid of a computer program the intensities of the satellite lines were corrected for the overlap with the main line. The two satellites and the main line were fitted using three gaussian derivatives, with two adjustable parameters namely, the amplitude and width. The position of the satellite lines were fixed at approximately $g_n\beta_nB$ from the main line. The ratio I_{sat}/I_{main} corresponding to zero power is obtained by extrapolation from a plot of I_{sat}/I_{main} vs. microwave power (fig.(2)), in order to eliminate saturation effects. This ratio was used in eq.(1) to get r. For the $M_I = 3/2$ line, when the magnetic field is parallel to c^* axis, and B = 0.3214T, I_{sat}/I_{main} is 0.065. Assuming that only one closest hydrogen is involved in spin flip, θ , the angle between the hydrogen closest to metal centre and the magnetic field at the aforesaid orientation is 129.6°. The r calculated from eq.(1) is 2.28Å. The separation of satellite from the main line at 0.3214T is 0.45mT. Using this value in eq.(2) $r_{\Delta E}$ was found to be 2.23Å. Since r is comparable to $r_{\Delta E}$ the assumption that only one proton is involved in the spin flip transition is justified. The considerable difference in the values of r obtained from spin flip studies and from crystal structure (3.04Å) is because the measurements were made at X-band frequencies, where the
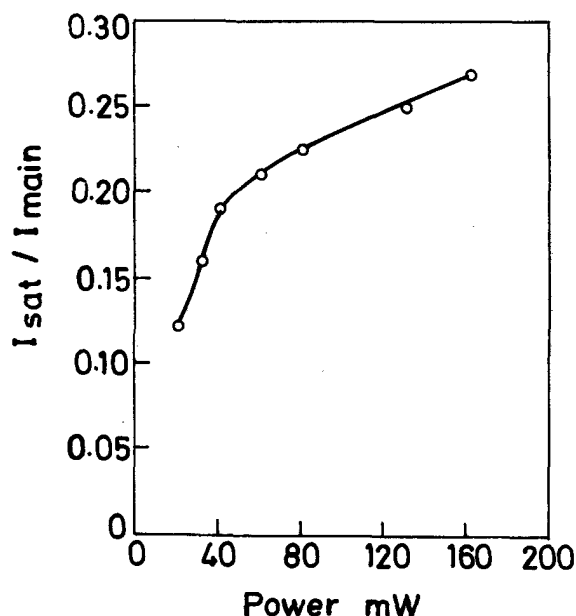
Fig. 2 A plot of I_{sat}/I_{main} as a function of power at room temperature

following factors lead to a higher than expected I_{sat} value [8], which results in a lower value or r: (i) for X-band, the high field approximation is not valid and this may introduce an error by a factor of 2 in the calculation of I_{sat}; (ii) insufficient resolution of the satellites at X-band. Apart from these, contribution from the isotropic hyperfine coupling between the electron and the proton would lead to error both at X- and Q-band frequencies [2] resulting in a higher than expected satellite intensity.

I_{sat}/I_{main} ratio: In order to explain the differential saturation exhibited by spin flip satellites, Shimizu [9] took into consideration differences in the microwave induced transition probability and the lattice induced transition probability between the main and the satellite lines and calculated the differential saturation expected for different mechanisms assumed for spin lattice relaxation. For a dilute two spin system as is the case for the one under study,

differential saturation can be used to distinguish between two different spin lattice relaxation mechanisms. These are the radial modulation of the crystal field by lattice modes or by dipolar coupling between the electronic and nuclear spins (case a) and the angular modulation of the dipolar coupling to the lattice protons (case b). Case "a" is characterised by two fold increase in the I_{sat}/I_{main} in going from low to high powers. This mechanism is commonly observed for spin systems having significant departure from free g, indicating substantial orbital contribution to the magnetic moment thus making it possible for the spins to feel the lattice vibrations. If I_{sat}/I_{main} changes by a factor of 50 to 100 from low to high microwave powers, it is indicative of case "b" known to occur by intramolecular interactions. These conclusions arrived by Shimizu apply semiquantitatively to actual multi level systems.

A plot of $2I_{sat}/I_{main}$ as a function of microwave power at 116K and 66K is shown in fig.(3). Here $2I_{sat}$ refers to the sum of the intensities of both the satellite lines. The ratio $2I_{sat}/I_{main}$ changes by a factor of about 6 in going from low to high powers at 116K so that the dominant mechanism here for the

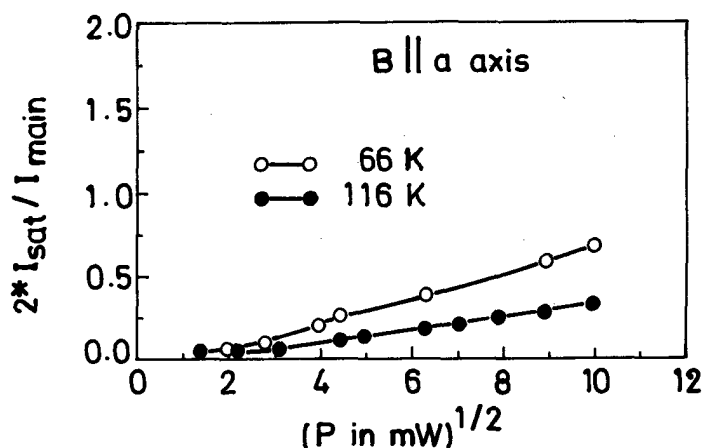**Fig. 3** A plot of $2 \cdot I_{sat}/I_{main}$ as a function of power at two different low temperatures

electron relaxation is via the spin-orbit and orbit-lattice interactions (case "a"). This mechanism is very much possible in this system, since the g factor is quite anisotropic and deviates considerably from free g. But at 66K $2I_{sat}/I_{main}$ changes by a factor of about 14.7 which means that a combination of both mechanisms, the radial and the angular modulation of the dipolar coupling, operate. The latter mechanism seems to dominate as the temperature is lowered. In fact at a temperature lower than 100K this seems to be the dominant mechanism, over shadowing the radial modulation. There are three other interesting observations: (i) as temperature is lowered, for the same microwave powers, saturation effects are greater for the main line while the satellites gain intensity; (ii) It is interesting to note that there is no saturation of the main forbidden hyperfine lines from ^{63}Cu; (iii) the observation of spin flip transitions seems to be a common phenomena among the dithiolene complexes [4-6, 10-11] and hence it is inferred that some interesting property and/or electronic structure of the dithiolenes must be able to explain the mechanism for the general observation of these high intensity spin flip lines in dithiolenes. More detailed work is under progress.

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