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Localized Spins in *p*-Phenylene Diamine-Bromanil Complexes†

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In a number of studies of the electron magnetic resonance spectra of donor-acceptor charge transfer complexes,[1–3] the temperature dependence of the absorption approximately follows the Curie Law, $\chi \sim 1/T$ at temperatures near that of liquid nitrogen. It is generally assumed that in this temperature region most of the absorption is of extrinsic origin. Indeed, Pott and Kommandeur[4] showed that such effects could be produced in their samples by varying the method of preparation. The magnitudes of the absorption are outside the limits expected for impurities. Hughes and Soos[5] have proposed that the low temperature absorption in *p*-phenylene diamine-chloranil is due to molecular chains of only finite length with an odd number of radicals. The purpose of this note is to report that in some samples of *p*-phenylene diamine-bromanil the number of spins appears to be constant over a wide range of temperature, from 77°K to 300°K and that the spins appear to be localized on bromanil radical ions.

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Microcrystals of *p*-phenylene diamine-bromanil were precipitated from a mixture of hot solutions of the two constituents in benzene.[6] The *p*-phenylene diamine was from Eastman Organic Chemicals, the bromanil from K. & K. Laboratories. EMR absorption spectra were measured on a reflection homodyne spectrometer at 9 GHZ.

The crystals were not large enough for single crystal measurements. Measurements on a collection of microcrystals in a nitrogen atmosphere gave a spectrum at 77°K which is shown in Figure 1. A spectrum of this shape is characteristic of powder samples of a material with a cyclindrically symmetric g tensor.[7,8] It is possible with the assumption of cylindrical symmetry to extract the values of $g_{\parallel}$ and $g_{\perp}$ as described by Searl *et al.*[8] The g values for this *p*-phenylene diamine-bromanil sample at 77°K are $g_{\perp} = 2.014 \pm 0.002$, $g_{\parallel} = 2.001 \pm 0.002$.

Hughes and Soos[5] point out that the observed g values of *p*-phenylene diamine-chloranil are the average of those for the two radical ions of the complex as expected if the spin excitations are mobile and spend equal time on both types of radical. Since the g anisotropy of the radical ions is due largely to spin orbit coupling[9] which increases with atomic number and therefore should be higher for bromanil than for chloranil, $g_{\perp}$ for the bromanil radical ion should be significantly higher than for chloranil. Solution measurements of the bromanil radical ion give an average g value,

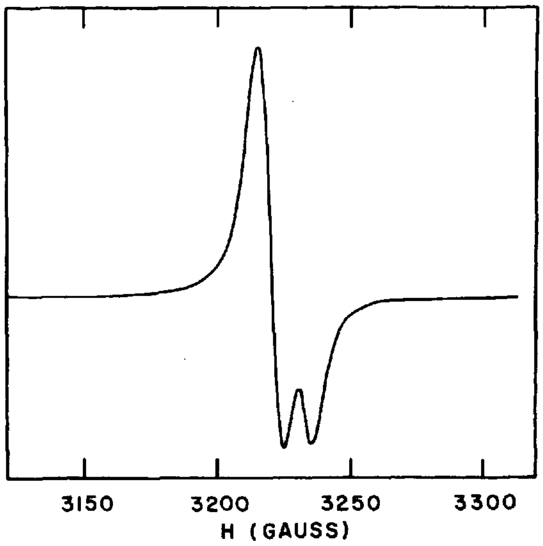

FIGURE 1 First derivative EMR spectrum of *p*-phenylene diamine-bromanil microcrystals at 77°K.

$g = (g_{\parallel} + 2g_{\perp})/3$ of 2.0084[10] and 2.0088.[11] If $g_{\parallel}$ is assumed to be 2.0023[5], $g_{\perp}$ for the bromanil radical ion should be between 2.011 and 2.012, compared with 2.0085 for the chloranil radical ion.[5]

If the spins in the *p*-phenylene diamine-bromanil were non-localized, an average $g_{\perp}$ of about 2.007 would be expected. Sato *et al.*[12] report a value of 2.0087 at 300°K, close to that expected for mobile spins. The value for $g_{\perp}$ for this investigation at lower temperatures is closer to that expected for the bromanil negative ion which suggests that the observed spins are localized on these ions. Similar effects have been observed in *p*-phenylene diamine-chloranil. Hughes and Soos mention the presence of narrow lines due to spins localized on isolated chloranil anions in some crystals of *p*-phenylene diamine-chloranil at temperatures below 200°K.[5]

The temperature dependence of the spin resonance absorption is shown in Figure 2. In this figure the product of the absorption and temperature is plotted versus temperature. It can be seen that the product of spin concentration and absolute temperature is essentially constant and thus the Curie law approximately satisfied. In Figure 3 are shown the line shapes for various temperatures. The change in line shape is probably due to loss of resolution caused by increased spin-lattice relaxation. At room temperature the average g value is still 2.010 ± 0.002 which gives $g_{\perp} = 2.014$ if $g_{\parallel}$ is again assumed to be 2.0023.

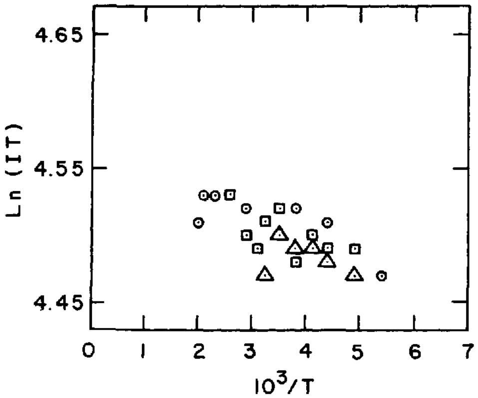

FIGURE 2 A plot of the logarithm of the product of integrated intensity and absolute temperature versus reciprocal temperature. Circles, squares, and triangles refer to three different samples.

We may summarize these results as follows. For certain samples of *p*-phenylene diamine-bromanil the anistropy of the g value can be described by an axially symmetric g tensor with $g_{\perp} = 2.014 \pm 0.002$, and $g_{\parallel} = 2.001 \pm 0.002$ over the temperature range 77 to 300°K. Furthermore the number

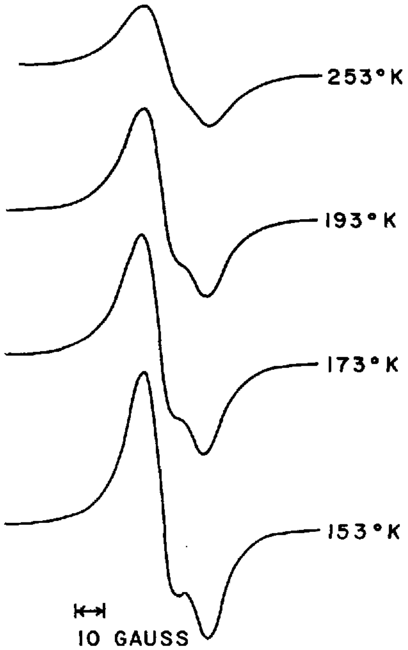

FIGURE 3 The EMR spectre of *p*-phenylene diamine-bromanil microcrystals at several temperatures.

of spins is approximately independent of temperature. The value for $g_\perp$ is much larger than the average of $g_\perp$ for *p*-phenylene diamine and bromanil radical ions, the value which would be expected for a mobile spin excitation, but is close to the value for the bromanil ion. Thus the spins appear to be localized on bromanil ions over the entire temperature range studied. The bromanil ions which are acting as traps are undoubtedly extrinsic, perhaps located at crystal defects or resulting from imperfect stoichiometry of the compound.

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