

A Pilot Study of Paramagnetic Resonance Centres in Selected Argyle Diamonds*

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Abstract

Seven rough octahedral diamonds of good quality were obtained on short loan from the Argyle mine and studied at room temperature for paramagnetic centres using a Varian E-12 X-band spectrometer. The specimens were all ~ 2 carat in weight and comprised two whites, two pinks (one slightly darker), one 'champagne' and two 'cognacs'. The following centres were identified: single N centre (P1) and the aggregated 3N centre, (P2). Two other centres were found: a centre at $g = 2.0028$, with no discernible hyperfine structure, the intensity of which was colour-correlated; and a centre with two discernible hyperfine lines and a similar g -value with a different splitting from the single N-centre. Crystal rotation showed an axial (111) spin Hamiltonian with $A_{\parallel} = 41.4 \times 10 \text{ cm}^{-1}$, $A_{\perp} = 34.6 \times 10^{-4} \text{ cm}^{-1}$, with only one of the four equivalent sites occupied, which perhaps indicates that plastic deformation plays an important role in the formation of these centres. All centres behaved differently with respect to saturation. These results are different to those obtained elsewhere on early Argyle diamond specimens. It is hoped that further analysis of these electronic centres in diamond will give clues regarding the nature of the colour centres.

1. Introduction

Diamonds from the Argyle mine in Western Australia differ from those from other mines in certain respects. Firstly, they come from Lamproite pipes, not from Kimberlite pipes, and these differ in shape. Secondly, there are many good quality coloured diamonds, as well as (clear) white ones: light brown ('champagne'), dark brown ('cognac'), rare pinks and blues, and so studies that may reveal the origins of these colours are intrinsically worth while.

The use of electron paramagnetic resonance (EPR) to study induced and natural defects and natural impurity centres in diamonds commenced in the 1950s (e.g. Griffiths *et al.* 1955), and this early work has been reviewed by Loubser and van Wyk (1978). Nitrogen is a common impurity in diamonds and so consequently various N impurity centres and defects have been studied. The Argyle diamonds generally contain less N than those from other mines, but could possibly contain other defects (Chapman and Humble 1992). Hence, a study of Argyle diamonds using EPR was undertaken in the hope of passing from the known defect spectra, especially for N centres (see Fig. 1), to previously unreported centres. EPR studies reported by Humble at the 1988 Diamond Conference in Cambridge (personal

* Paper presented at the Festschrift Symposium for Dr Geoffrey Fletcher, Monash University, 11 December 1992.

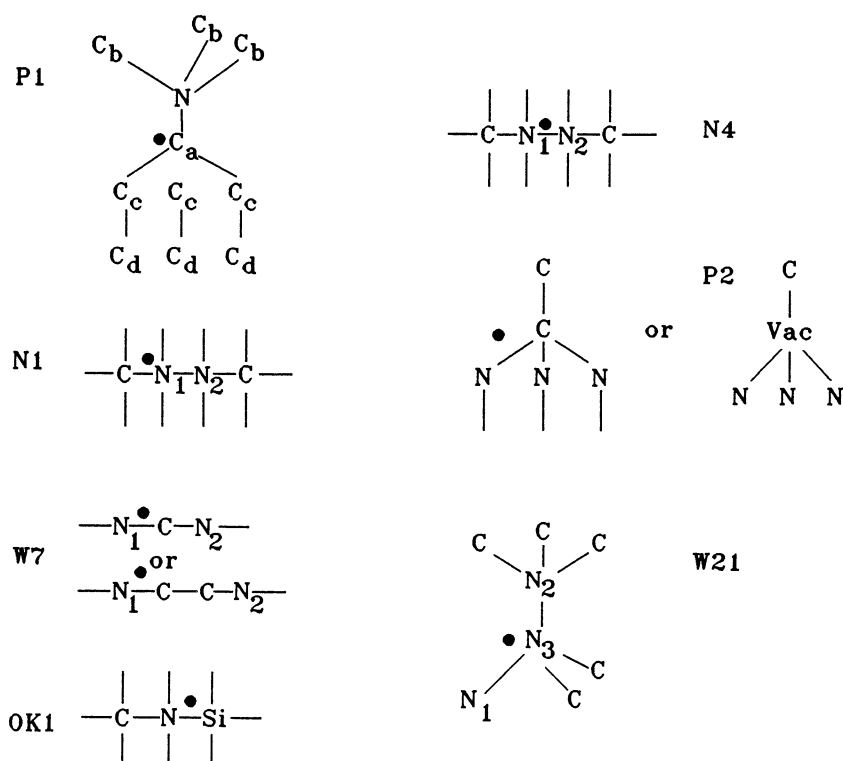


Fig. 1. Schematic representation of some N-associated centres that have been identified by EPR (after Loubser and Van Wyk 1978). The tetrahedral nature of the bonding in diamond should be borne in mind when interpreting these sketches.

communication) had revealed only the N and the 3N centres; further, this work was undertaken by the adiabatic rapid passage method, using dispersion mode, in order to increase signal-to-noise ratios (Campbell 1987). Our work was undertaken in the normal CW mode.

2. Apparatus

The EPR measurements were carried out using a Varian E-12 X-band (~ 9 GHz) spectrometer, some 15 years old. The sensitivity had degraded by a factor of ~ 10 over the years: the current sensitivity is estimated to be $\sim 10^{11}$ spins ($S = \frac{1}{2}$: linewidth 0.1 mT). Because the diamonds were comparatively large and would only just fit inside the resonant cavity, accurate rotation of the specimens was not possible. Despite the size of the diamonds, the signal-to-noise ratio was not large, except for one of the centres (or combination of centres) present. Further, the size of the diamonds excluded the use of the Varian liquid- N_2 cooling system. These conditions limited the information obtainable on the new centres discovered.

3. Specimens

Seven recognisably octahedral good-quality diamonds of approximately 2 carats each were obtained from the Argyle Diamond Company. The colours were two white (clear), one 'champagne' (light brown), two 'cognac' (dark brown), and

two pinks, one slightly darker than the other. One of the whites and one of the cognacs had in fact formed a single stone when found: the regions of different colour were separated by the Argyle Diamond Company for research purposes.

4. Results

The white specimens showed the single N (P1) centre lines and those from the aggregated 3N (P2) centre. These saturated at different microwave powers and could be clearly identified by their rotational behaviour, despite the accuracy limitation of the rotational system, because of the recognisable octahedral features of the diamond crystals.

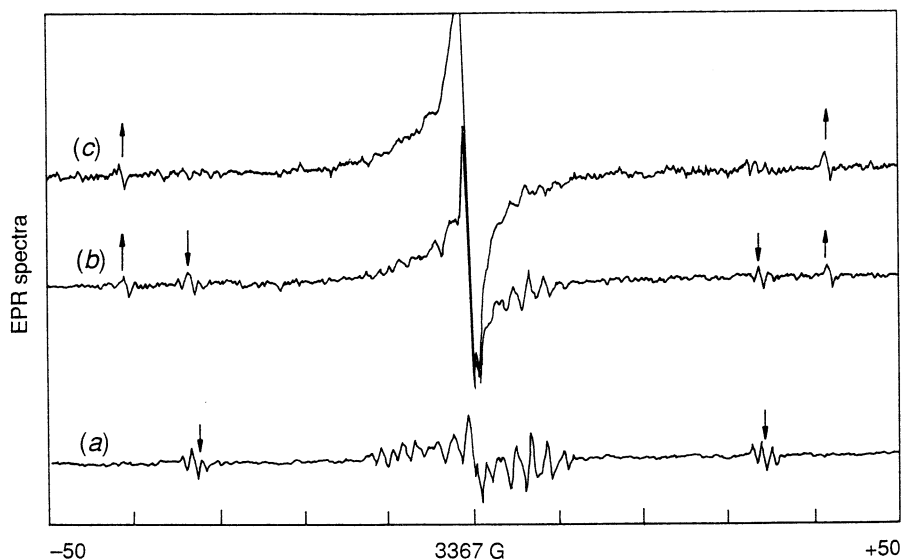


Fig. 2. Behaviour of the EPR spectrum of a 'champagne' Argyle diamond, for dc magnetic fields perpendicular to the 001 direction, with incident microwave power: (a) 0.01 mW; (b) 0.1 mW; and (c) 1.0 mW (1 G = 0.1 mT). For curve (a), the central series of lines (visible throughout) belong to the P2, or 3N centre, with the central (colour-correlated) line starting to emerge, and the single N (P1) centre lines (arrows down). Curve (b) shows all centres: 3N (P2), colour-correlated, single N (P1) centres (arrows down) and unknown centre (arrows up). For curve (c), the P1 centre has now been totally saturated, leaving the unknown centre (arrows up), and the colour-correlated centre, with the structure of the P2 centre having been essentially destroyed.

All coloured stones showed these same spectra, with approximately the same intensity. As well, they showed a new centre with lines outside those of the single N centre, not correlated with depth of colour. Whereas rotation of the crystal away from 100 split the P1 lines into four equivalent sites, the lines of the new centre remained single, indicating that the spectrum arose from a centre with one site preferentially occupied. A careful rotation study showed that the centre had axial symmetry about one of the (111) directions, with $A_{\parallel} = 41.4 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = 34.6 \times 10^{-4} \text{ cm}^{-1}$. The line intensity varied somewhat with direction, broadening significantly parallel to the (111) axis. This new centre also behaved differently, with regard to saturation, from the previously mentioned centres. This can be seen in Fig. 2, which shows the saturation

behaviour of the 'champagne' crystal's ESR spectrum, with respect to microwave power. Finally, all coloured stones showed a single apparently unstructured line at $g = 2.0028$, again behaving differently regarding saturation, the intensity of which was colour-correlated (at the same level of power). This signal was more intense in the darker pink specimen than in the lighter pink, and more intense in the cognac than in the champagne: the intensities in the darker pink and the champagne were approximately equal. The behaviour of this line with respect to saturation is also shown in Fig. 2.

5. Discussion

These results are different from those reported by Humble (personal communication, 1988) for ESR spectrometry on *early* Argyle diamonds. This can be explained by postulating that the physical and solid-state chemical characteristics of diamonds may change as we proceed to extract them further down the Lamproite pipe. What is required for further study of the two newly discovered centres is greater sensitivity of the spectrometer, and pulsed EPR spectrometry. Both these requirements will be met by the Bruker EPR spectrometer soon to be installed in our laboratory. The CW sensitivity will be ~ 100 times our present sensitivity, so smaller samples could be used with a consequent increase in the accuracy of rotational alignment. The fact that the various centres all behave differently as regards saturation is convenient, as with the appropriate pulse sequences and widths it should be possible to target each centre separately, because of the clearly different combinations of spin-lattice and spin-spin relaxation times.

It has been suggested (Chapman and Humble 1992) that the colour of Argyle diamonds is due to plastic deformation during and after their formation, creating defects. If these defects involved 'dangling bonds', essentially free radicals, this could explain the structureless central line, centred at $g = 2$, which is colour-correlated. Such a line has been reported previously, and so interpreted, by Shcherbakova *et al.* (1975). The non-isotropic distribution of centres throughout diamond has also been observed before, particularly with the N4 and W7 centres (Loubser and Van Wyk 1978). The spin Hamiltonian for the new centre we report here differs from those for N4 and W7, but the single site occupancy can be seen to be consistent with the samples having been plastically deformed.

Acknowledgment

We are very grateful to Dr John Chapman of Argyle Diamonds for so kindly supplying the specimens for examination.

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