

# Determining the Activation Energy of $N_s^0$ Charge Migration in Natural Diamonds

J Labram, G Ross, S Felton and M E Newton

Department of Physics, University of Warwick, Coventry, CV4 7AL

## Introduction

As the price of synthetically grown diamond falls, its wide-spread use in industry is becoming more of a significant possibility. Diamond has many potential uses including semiconductor devices, surgical tools and high-strength windows. Understanding the properties and behaviour of impurities in diamond is essential for the extensive use of this remarkable solid to be realised.

Pure diamond is a single crystal of carbon atoms. During the formation of diamond, nitrogen atoms often take up substitutional positions within the crystal lattice, meaning that at a site where a carbon atom is expected, there is a nitrogen atom. Since nitrogen has one more electron in its outer shell than carbon, the impurity leaves a localised free electron. This electron gives rise to many interesting properties, some of which could one day allow diamond to be used in semiconductor devices or as a form of optical memory.

It is well known that the detected concentration of single substitutional nitrogen (often labelled  $N_s^0$ ) in some diamonds changes after the diamond has been heated or irradiated with light. The mechanism by which this charge transfer process occurs is not completely understood but is thought to be due to a quantum-mechanical tunnelling process whereby the electron is transferred from the  $N_s^0$  site to an unknown trap X after acquiring a certain amount of energy. The purpose of this study was to quantitatively investigate how the concentration of  $N_s^0$  changes after being heated and to determine the threshold energy at which this process becomes possible.

## Electron Paramagnetic Resonance (EPR)

The experimental work for this investigation was carried out on a Bruker EMX EPR Spectrometer (see figure 1). Electron Paramagnetic Resonance is a technique used to probe the local environment of free electrons in a sample and is entirely dependent on quantum mechanics.



Figure 1. The EPR Spectrometer used throughout this investigation.

Electrons (and all other particles) possess a form of angular momentum called spin. Spin is a conceptually difficult concept to understand and is best thought of as an intrinsic property like mass or charge. With the application of a magnetic field, the energy associated with each spin state splits, making it possible for the electron to make

a transition between the states. The energy associated with this transition is dependent on the sample properties and the applied magnetic field strength.

If microwaves whose energy match the transition energy are passed through the sample, the free electrons absorb the energy of the photons (particles of electromagnetic waves) and make a transition between states. After the microwaves have passed through the sample they are detected by a photodiode. By sweeping the wavelength (and hence energy) of the applied electromagnetic waves, a smaller signal will be detected when the microwave energy matches the transition energy. This will be observed as a trough at the correct wavelength in an intensity vs. wavelength plot. In reality it is easier to vary the magnetic field and keep the microwave frequency constant. From the shape of the detected trough the concentration of  $N_s^0$  can be determined.

## Experiment

Throughout this investigation three diamond samples were used, they are shown in figure 2. It was possible to heat the samples up to approximately 800K while they were inside the spectrometer.

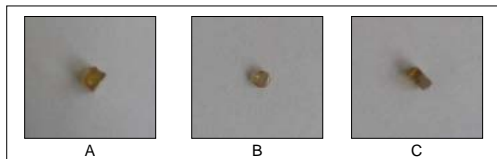


Figure 2. The three samples used for this investigation.

Each sample was heated for 5 minutes inside the spectrometer at a given temperature before being cooled back down to room temperature. An EPR scan was then taken and the relative concentration was then determined. The sample was then heated to a slightly higher temperature and the process was repeated.

The concentration of  $N_s^0$  is returned to its normal value after the sample is irradiated with light, the sample is then said to be in the "light" state. It was hence essential that the sample was shielded from all sources of light while this experiment was conducted.

## Results

An example of the data obtained is given in figure 3. The theoretical model here is quite simple. It is assumed the rate of change of  $N_s^0$  concentration in the sample is proportional to the concentration. Using the Arrhenius equation to determine the temperature-dependent rate constant, the relative concentration can be approximated by equation 1:

$$[N_s^0]_i = [N_s^0]_{i-1} - [N_s^0]^{(MIN)} \exp\left\{-\Delta t \exp\left(\frac{-E}{k_B T_i}\right) / \tau_0\right\} + [N_s^0]^{(MIN)} \quad (1)$$

Here  $[N_s^0]_i$  is the concentration of  $N_s^0$  at the  $i$ th data point,  $[N_s^0]^{(MIN)}$  is the proposed minimum  $N_s^0$  concentration,  $\Delta t$  is the heating time (300s in this case),  $E$  is the activation energy associated with the charge migration process,  $T_i$  is the temperature at the  $i$ th data point and  $\tau_0$  is a time constant. Using this equation, the parameters  $E$ ,  $\tau_0$  and  $[N_s^0]^{(MIN)}$  were varied using a fitting tool to match the experimental data as closely as possible. The parameters obtained are summarised in table 1.

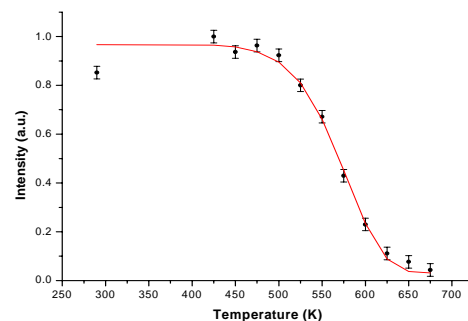


Figure 3. The relative concentration of the  $N_s^0$  impurity in sample B as a function of temperature. The black points represent the experimental values and the red line the theoretical model. The concentration was derived from an EPR scan taken at room temperature after the sample had been heated for 5 minutes at the given temperature.

Sample	E (eV)	Tau 0 (s)	NS0 Min. (a.u.)
A	0.5	0.6	0.06
B	0.7	0.0005	0.05
C	0.5	0.03	0.1

Table 1. The parameters found from fitting the theoretical model of equation 1 to the experimental data.

## Discussion

The values of  $E$  determined are approximately the same, suggesting that the activation energy of the  $N_s^0$  charge migration process is an intrinsic property of the impurity itself rather than of the specific sample. The energy required to excite the electron from the  $N_s^0$  site into the conduction band is 1.7eV<sup>[1]</sup>. Hence the process that is observed here is not due to this effect, this reaffirms the idea that this is a tunnelling process.

A previous study<sup>[2]</sup> on sample C used a different method whereby the time dependence of the decay process was investigated. The results from this study found the activation energy to be:

$$E = 0.26 \pm 0.02 \text{ eV}$$

This value, despite being of the same order of magnitude, is different from the value determined during this study. There are several possible reasons for this, one is simply that the model employed here (equation 1) is oversimplified, making it inadequate for determining  $E$  with any real accuracy. The model applied in the study previously mentioned<sup>[2]</sup> suggests that two decay processes are taking place, one fast and one slow. For this study the model involves just one decay and a minimum concentration. This inconsistency could be significant.

Another possibility is that the time of heating is not modelled correctly. The model used here treats the heating process as a step function. In reality it takes a finite amount of time to heat the sample up and cool it down. It normally took no more than 1 minute to heat

up and between 5-10 minutes to cool to below 290K, the higher the temperature the longer it took to cool. Also, in reality the heater overshoots the target temperature then oscillates around it before stabilising. A guess at the actual time dependence of the temperature is shown in figure 4, the red line is the 'real' temperature and the modelled temperature is the black line. Since the model is so dependent on temperature (through a double exponential) it is believed this approximation significantly limits the accuracy of the model.

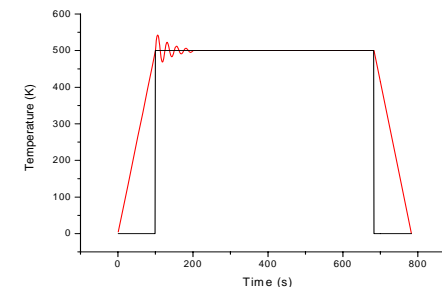


Figure 4. A guess at the time dependence of the heating process. The black line indicates the time dependence modelled in equation 1 and the red line is a guess at the actual time dependence.

## Conclusion

The fact the determined value of  $E$  was significantly less than 1.7eV is a good result and rules out the possibility that the charge migration is due to the electron being excited to the conduction band.

The exact value is of considerable interest but does not match the previously determined value<sup>[2]</sup>. The precise reason behind this inconsistency is unknown but could either be due experimental error or other reasons. Further study on this on this subject should clarify this matter. Investigation into other defects such as EPR-N3 and OK1 also present in these samples will reveal further clues as to the exact nature of this phenomenon.

## Acknowledgments

I would like to thank the Undergraduate Research Scholarship Scheme for funding this work, Gregory Ross for his contribution to this project, the Warwick Diamond Group for hosting me in their group and Mark Newton and Solveig Felton for their patience and support during this project.

## References

- [1] J. Davies, in 'Chemistry and Physics of Carbon' (R.W. Walker and P.A. Throver eds.), vol. 13 p1-143 (1977)
- [2] D. J. Twitchen, D. Phil. thesis, Oxford (1997)