Internal Fields in Diamond and Related Materials

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A thesis submitted to the Faculty of Science,
University of the Witwatersrand, Johannesburg,
in fulfilment of the requirements for the
degree of Doctor of Philosophy.

Johannesburg 1988

Abstract

The aim of this research was to develop the sensitive diagnostic method of Time Differential Perturbed Angular Distributions (TDPAD) using implanted fluorine (^{19}F) as the nuclear probe, and apply it to defect and impurity studies of diamond crystals, by detecting the internal electric field gradient (efg) at the impurity sites. Defects and impurities can substantially determine and modify the electrical and physical properties of materials. Such studies lead to theoretical advances and new materials. Diamond presents a unique system in which to perform these studies. The related Muon Spin Rotation (MSR) technique, which detects the local magnetic field at the muon residence sites, was also used to study the behaviour of the implanted hydrogen-like impurity.

The ^{19}F is recoil implanted into the diamond by a 4 MeV pulsed proton beam from an accelerator. The parameters describing the local efg (magnitude, asymmetry, distribution and orientation) at the residence sites of the implanted ^{19}F probes are measured by detecting the perturbed γ-ray angular distribution from the ^{19}F de-excitation. The efg reflects the local microscopic structure and dynamic processes. Measurements were performed as a function of crystallographic orientation, diamond type (naturally present defects and impurities) and temperature. Studies were also made of other carbon allotropes.

The accelerator pulsing facilities were improved by the stabilization of the chopper and the development of a buncher. Theoretical model functions were developed for the analysis of data for non-axially symmetric efg's in cubic single crystals.

Essentially two different residence sites for ^{19}F probe ions in diamond and its allotropes were found. The first (principal) site has a quadrupole coupling frequency of ≈ 60 MHz, and is well defined with near axial symmetry for the efg. The second (diffuse) site, has a lower coupling frequency, also near axial symmetry but a large spread in the efg. The efg is oriented along a $< 111 >$ crystallographic direction in both sites. The measured degree of polycrystallinity of the natural diamond lattice corresponded to certain defects and impurities in diamond.

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The efg data, in particular its temperature dependence, correlated well with the site assignments and theoretical predictions of cluster model molecular orbital calculations. The two sites for the ^{19}F impurity are identified as the tetrahedral interstitial and substitutional sites. The temperature behaviour of the substitutional site led to a charge transfer model for the dynamics of ^{19}F at this site. Host-impurity interactions were shown to be dominated by chemical effects. The temperature dependence of the efg supports the charge carrier governed dependence models for semiconductors. The MSR measurements pinned down the signs of the anisotropic hyperfine coupling constants describing a stable form, Mu*, of the muonic atom in diamond. This led to dynamical and structural insights into the transition yielding Mu*.

The ^{19}F TDPAD method has matured during the course of this research into a sensitive diagnostic technique, and a consistent picture of the ^{19}F impurity in diamond is emerging. The results are of importance to the general understanding of defects and impurities, especially in diamond, and interesting possibilities for future research are suggested.

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand. It has not been submitted before for any degree or examination in any other university.

16 day of March, 1988.

This thesis is dedicated to my wife, Geraldine.

CONTENTS

Acknowledgements

This work depended on the support and co-operation of many people. A very sincere thankyou to all the team at the Schonland Research Centre for Nuclear Sciences, who created such a genial working environment and who helped so unstintingly.

I feel proud and privileged to have been supervised by Professor Sellschop and Doctor Stemmet. I attribute my rapid progress, enjoyment and learning to the quality of their challenging supervision. I am indebted to Professor Sellschop, my first supervisor, for his round-the-clock availability for discussions, advice and inspiration. He is a veritable fountain of ideas. I have truly benefited from his vast knowledge and expertise, and his tremendous physical intuition combined with an original approach to problems in physics. It has been a pleasure working in a laboratory of international repute with an infra-structure of such high calibre professional technicians and equipment, and the Research Centre certainly owes its existence to his dynamic administration.

I am also indebted to my second supervisor, Doctor Stemmet. His meticulous approach to experimental detail and instrumentation together with his scientific vision was invaluable in my research. I owe to him my solid grounding in all aspects of thesis research. He guided me well, providing continual encouragement and always helping out with problems which arose. I feel very fortunate to have been the student of such an outstanding teacher.

It was a pleasure to have performed these experiments in close collaboration with two eminent physicists from other universities: Professor Bharuth-Ram and Professor Appel. Professor Bharuth-Ram is a very stimulating and generous colleague who has collaborated closely with us. I value his regular visits and thank him for enriching the team, especially in the area of data interpretation. I had many inspiring discussions with Professor Appel. My visit to his laboratory was an enlightening experience and resulted in many useful discussions with his colleagues, especially Dr. Thies and chats with his students, especially Dr. Then. My thanks to them for explanations of the finer points of TDPAD experiments and computer data analysis.

I would also like to extend my appreciation to:

Collaborators in the related MSR experiments from the Zurich MSR-group, led by Professor W. Kundig. I am grateful to Bruce Patterson, Walter Odermatt and the rest of the team for my solid grounding in the computational simulation and interpretation of spectra;

Roger Fearick for many useful discussions, suggestions and sound computing advice. His efficient, menu-driven computer-controlled data aquisition system was indispensable with its many advanced primary spectra-reduction facilities. I am indebted to him for always being available to bounce ideas around with me;

Trevor Derry for his help with interpreting Laue patterns and who together with Johan Prins clarified many aspects of ion-implantation and damage in diamond;

Other scientists in the University and the Research Centre - Harold Annegarn, Udo von Wimmersperg, Vladimir Hnizdu, Darryl Comins, John Watterson, Rex Keddy and Uri Karfunkel who, although not directly involved in my project, were always available for discussions relating to equipment and help with aspects of their fields which intersected with mine. They contributed to a supportive atmosphere, allowing an enriching cross-pollination of ideas.

My fellow students - Alfred Hoernle, Elias Sideras-Haddad, Avin Pillay, Sangiv Shrivastava and other student colleagues for all their help with running the dark shifts and for our day-to-day problem solving together;

Ted Lowther, Wynand Verwoerd and Piotr Badziag (Unisa) for our excellent discussions and collaborations on cluster calculations.

Physics research is not possible without highly skilled technical back-up. Credit for the high standard of research at the Schonland Research Centre for Nuclear Sciences goes to our technical team. It is with justifiable pride that I acknowledge their help and support, as I know we are envied by many overseas laboratories. I would like to make special mention of:

Our expert from the electronics development laboratory - Hugo Andeweg. Without his extremely high standard of professional excellence, the experiment would not have been possible. His modifications to NIM electronic modules enhanced their capability, while his ingenious design of the detector bases, the "halo" start detector, the chopper, the buncher and various control modules made him an invaluable member of the research team. Many of his designs have resulted in publications. Without exception, his components worked at first switch-on. His help in debugging many electronic problems contributed to very clean spectra. My grateful thanks also go to Gidu Goldstein and the rest of the electronics staff;

John Beer, our 24-hour-a-day technical supervisor, who kept the machine on the air and also gave me a great deal of electronic advice and help in the many hours I spent in discussion and consultation with him;

Franz Rehm for the high standard of the vacuum equipment on the accelerator and for his all-round technical assistance;

The late Henk Kleynhans who taught me the finer points of the art of tuning a stable beam;

The now retired Lieb Verga and Alex Gray, and the rest of their team, Ian McKowen, Ian McQueen, for their expertise in the accurate construction of the many mechanical parts that were necessary;

Mick Rebak from the techniques laboratory for his precision cutting and polishing of the diamonds and the preparation of all the targets as well as the design and construction of the high temperature target mount. Our frequent discussions were also very useful to me;

Rory Leahy, who developed the computational system of the Research Centre. I am deeply grateful for the many hours he spent training me to use computers as an analytical tool and for the provision of black box routines.

I am grateful to the participants of the 1987 Nato School held in Portugal: the senior participants, who in between sessions, were living encyclopaedias of knowledge and enriched my background considerably, while I gained many insights from my discussions with the junior participants;

I record with appreciation the financial support of the Foundation for Research Development through the comprehensive grant of Professor JPF Sellschop, and the financial support and the provision of sample materials from Messrs de Beers Industrial Diamonds (Pty) Ltd. I wish to pay particular credit to the ongoing encouragement of Drs. HB Dyer, C Phaal and R Caveney. The University of Witwatersrand has also provided financial support and facilities.

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