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Internal Fields in Diamond and Related Materials

Simon Henry Connell

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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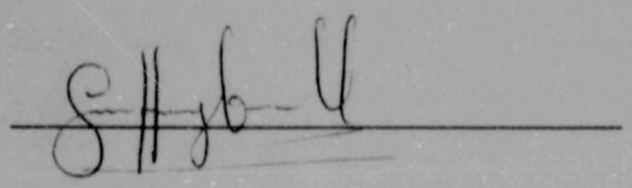
The efg data, in particular its temperature dependence, correlated well with the site assignments and theoretical predictions of cluster model molecular orbital calculations. The two sites for the ^{19}F impurity are identified as the tetrahedral interstitial and substitutional sites. The temperature 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.

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