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Internal fields in diamond and related materials

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CHAPTER 1.
INTRODUCTION

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Motivation

General

This thesis reports on defect and impurity studies of diamond using nuclear hyperfine methods. In particular the techniques of Time Differential Perturbed Angular Distributions (TDPAD) and Muon Spin Rotation (MSR) were used. This type of research is described as nuclear-solid state physics as it applies nuclear techniques to investigate problems in solid state physics. It is well known in solid state physics that the electronic, physical or optical behaviour of a material is determined, to a large extent, by the particular defects and impurities present in the crystal lattice of the material. The understanding and tailoring of the defects and impurities allows fabrication of materials with practically any property the designer could wish. There is consequently tremendous academic interest in the microscopic structures of materials, the defects and impurities therein, their interactions, and the field of implantation damage and damage annealing, since this is often how defects and impurities are introduced or controlled. On the theoretical side this has involved the latest techniques of quantum mechanics and group theory to describe the solid state systems. On the experimental side a large armoury of microscopic diagnostic tools has been developed, particularly through the application of the nuclear sciences to solid state research. In general the information concerning the lattice under investigation comes second hand, i.e. as seen by the effects on probing beams or particles. This has necessitated corresponding theoretical advances in the field of ion-solid interactions. Solid state information has to be extracted from spectra by computer programmes based on the theory of these interactions. Besides the tremendous academic interest of such research the goal is clearly very practical, and there are already many new technologies which have arisen from it.

Defects and impurities in Diamond

This thesis thus represents a small contribution to this rapidly expanding field. The microscopic structure of a particular material, diamond, is studied, especially with regard to the behaviour of defects, impurities and implantation damage processes. Recently diamonds have been successfully doped with boron to become p-type semiconducting material [Pr 88]; however the understanding of and ability to control this pro-

cess is not yet complete. In addition diamonds are naturally "radiation hard", and have an excellent thermal conductivity. They are idealy suited to specialised applications which require these characteristics for electronic components. Besides its unique physical properties, diamond represents the high band gap or insulating extreme of the mono-elemental semi-conducting range of materials. The idealized lattice has an extremely simple structure, although natural diamonds can contain many defects and impurities. For many theoretical treatments they represent an approximation to the strong bonding limit. This makes them a proto-type material for many studies of defect and impurity systems. The extremely high Debye temperature allows one to neglect some thermal effects, simplifying interpretation of data. An improved understanding of diamond growth will facilitate their fabrication. Control of this process would allow extensive use of micro-diamond layers as hard coatings or specialized optical coatings. Combining the techniques which produce ultra-thin diamond layers with those which modify the electrical behaviour of the diamonds is expected to lead to solar cells, and other specialized chips.

Most of the research has relied on the Time Differential Perturbed Angular Distributions (TDPAD) technique. These measurements were performed using the tandem Van de Graaff accelerator at the Wits-CSIR Schönland Research Centre (SRCNS) for Nuclear Sciences at the University of the Witwatersrand. The ^{19}F ion was chosen as the nuclear probe, and it was recoil implanted into the host lattice, representing an implanted impurity. The electric field gradient (efg) parameters of magnitude, asymmetry, distribution and orientation were determined by measuring the quadrupole interaction between the probe and the local efg at the residence site of the probe. The efg data was measured as a function of crystallographic orientation, concentration of natural nitrogen and boron impurities and lattice integrity (diamond type), and as a function of recoil implantation temperature. In addition studies were made of some other carbon allotropes. The related Muon Spin Rotation (MSR) technique was also used to study the behaviour of the hydrogen-like impurity. These measurements were performed at the Swiss Institute of Nuclear research (SIN) near Zürich in Switzerland. The next section maps out the plan of this thesis where details regarding the application of the hyperfine techniques, the reduction, analysis and interpretation of the data are described.

Plan of Thesis

Since TDPAD is the dominant research method in this work, it has recieved much more attention, and the first five chapters are devoted entirely to it.

Chapter 2 on Research methods situates the TDPAD technique amongst the other nuclear techniques and describes the principles behind the it. It explains the choice of ^{19}F as probe ion and discusses those properties of the diamond lattice which are relevant to the interpretation of the data. Since nuclear techniques are to a certain extent disruptive of the environment they are supposed to be studying, this effect is also carefully discussed. These considerations are vital for interpretation of the TDPAD spectra in the sections to follow.

Following this, Chapter 3, outlines the theoretical basis of the PAD technique, and describes the reduction and analysis of the data. Although much of this work appears in the standard texts, this section is detailed since the theoretical treatment presented for the specific case of single crystal targets with non-axially symmetric efg's and also non-negligible second order anisotropy coefficients is broader than has been presented before [Co 87]. Also a powerful computer analysis program was developed for handling in-beam TDPAD spectra where there is a high background and relatively poor time resolution.

Chapter 4 describes the experimental set-up and details the development of equipment which occurred. Details regarding target characterization, equipment testing and data reduction are also included here.

Most of the work in this thesis is published, awaiting publication, or has been recently submitted for publication. The results and conclusions are therefore presented as a collection of six papers. These form the fifth chapter. This method is made possible by the fact that the six papers form a well rounded story which is to a large extent an inter-related whole. The papers clearly reflect the progress in our understanding of the problem of the ^{19}F TDPAD probe in diamond, and the later papers become gradually more diagnostic, rather than being simply an evaluation of the ^{19}F probe itself. An introduction to this chapter describes this process and serves to give coherence to this chapter.

The sixth chapter covers the MSR results obtained for diamond. The focus here is on the results and the interpretation thereof. The description of the method and its theoretical background is only briefly sketched out as the experimental principals bear many similarities to the TDPAD case.

Chapter 7 summarizes the results and conclusions of its precursor not necessarily in the order in which they occurred. This is a most important chapter which contains the body of information presented in this thesis. The ^{19}F TDPAD method has matured, yielding many exciting results, and some suggestions are made as to future studies.

The Appendix contains details which would have interrupted the flow of the thesis had they been in the main text. The table of contents is self explanatory here, except for the item on electron - positron scattering. This describes a recent search for resonant production of a new particle in $e^+ - e^-$ scattering. Since six months were spent by the author on this subject which led to the production of three papers it was decided to include a short description of it in the Appendix.

CHAPTER 2.
RESEARCH METHODS (TDPAD)

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Introduction

The TDPAD method

Time Differential Perturbed Angular Distributions (TDPAD) is a nuclear spectroscopic technique usually applied in investigations in solid state physics. It is a special case of the more general technique of Perturbed Angular Correlations (PAC). In fact there is a variety of microscopic investigative techniques which has resulted from the application of nuclear sciences to materials problems. Some of these are Ion Channelling and Rutherford Back Scattering, the more traditional Nuclear Resonance techniques, the Mössbauer Effect and Positron Studies. Each of these techniques has advantages and disadvantages relating to its range of probes, samples that can be studied (or particular microscopic locations within the sample), physical parameters that can be determined, and sensitivity of the method. The relative merits of these methods are regularly reviewed in the literature [Ka 79, Ko 84, Na 87]. In general it is difficult to grade them as technical and theoretical developments are continuously enhancing their power. More often than not an armoury of techniques is necessary for the complexity of the problems in solid state physics.

The PAC methods are based on the well-understood dependence of the emission direction of de-excitation radiation on the nuclear spin orientation of a decaying nucleus. This is a direct consequence of the conservation of angular momentum and the fact that the angular momentum of the radiation is correlated with its direction of emission. If a probe nucleus can be prepared in an isomeric state with a non-uniform population of the magnetic substates, then its nuclear spin will have a specific orientation, and the spatial intensity pattern of the de-excitation radiation will be anisotropic. The PAC method pertains when the decay is via a double cascade. The non-uniform population of the magnetic substates is achieved by selectively observing the second radiation only if the first radiation is also observed. This ensures that the second radiation is emitted from an intermediate state of known nuclear spin orientation, and the second radiation is thus correlated with the first. The resulting anisotropy contains information on the spins and multipolarities (and hence parities) of the transitions involved. Previously this technique of angular correlations was used to study the decay schemes of the radioactive nuclides.

When the alignment of the substates is achieved by excitation of the level via a nuclear reaction involving a projectile with a known incident direction, the resulting anisotropy is known as an angular distribution. If the excited nuclear probe is inserted into a host lattice, then any hyperfine fields in its neighbourhood will lift some or all of the degeneracy of the magnetic substates and perturb their relative populations. In fact the relative populations of the substates vary periodically with frequencies given by the level splittings. This causes the orientation of the nuclear spin to change in a periodic way. This is classically described as a precession of the nuclear spin axis in the presence of a field. Obviously the anisotropic distribution of the de-excitation radiation pattern, which is tied to the nuclear spin, will also have to rotate. When this rotation is observed with time, the method is known as Time Differential PAD. Information concerning the perturbing field, and thus the microscopic environment, is extracted by computer analysis of the time differential radiation pattern. Subsequent sections describe in more detail the quantitative theoretical aspects and experimental arrangements of this method.

TDPAD is relatively new technique and was born of the recently developed ability of particle accelerators to produce high quality pulsed beams of almost any heavy ion. This fast growing technique presents a number of advantages. Firstly, the variety of probes is greatly enhanced, reflecting the variety of nuclear reactions which may be used to produce the probe. It is becoming possible to probe the whole of the periodic table with the whole of the periodic table [Vi 87, Le 87]. Secondly the method of introduction of the probe into the host lattice under investigation complements existing methods. TDPAC has been used extensively in metals where probes may be inserted during a molten stage of fabrication. This possibility does not always exist for semiconductors and specifically not for diamond. The in-beam TDPAD method is a singles counting experiment as opposed to the $\gamma - \gamma$ coincidence counting of the PAC methods, and this allows a substantially more dilute probe concentration. The final advantage is the time window aspect of the TDPAD method. This is discussed below for the case of ^{19}F in diamond. In practice different time windows are available through the choice of probe.

In this research the probe is ^{19}F which is introduced into the (diamond) host lattice by recoil implantation. A proton beam simultaneously excites the 197 keV state of the ^{19}F and recoil implants it into the host lattice under investigation. The ^{19}F ions are

derived from a film of CaF_2 evaporated onto the upstream surface of the target host lattice. The isomeric state of the ^{19}F probes is aligned with respect to the incident beam direction. In this case the relevant hyperfine field which perturbs the anisotropic decay pattern is the electric field gradient (efg) at the residence site of the ^{19}F probe ion. The magnitude, asymmetry, distribution and orientation of the efg at the residence site of the probe ion is extracted by analysis of the TDPAD spectra. The efg parameters are determined by the local charge distributions in the lattice which are in turn determined by the microscopic geometrical arrangements and the various interactions. In this way, microscopic information on lattice structure, defects, impurities and their interactions may be investigated as functions of certain macroscopic parameters which may be varied, such as temperature or impurity concentration.

The ^{19}F probe ion

By 1987 49 different nuclei had been used as PAC probes [Vi 87, Le 87]. However ^{19}F has several properties which make it eminently suitable :

- its second excited state at 197 keV [Aj 87] has a quadrupole moment Q = 0.072(4) b [Mi 87]. Since the expected efg for diamond is $\approx 10^{18}$ Vcm^{-2}, the quadrupole interaction frequencies will be $\approx$ 30 MHz, which are observable to a few oscillations since the lifetime of this state is $\tau = 128$ ns.

- The spin and parity of this state is $\frac{5}{2}^+$. This is large enough to allow observation of the efg asymmetry as well as the efg magnitude, though still small enough to facilitate analytic diagonalization of the quadrupole interaction matrix [Ka 73].

- Further, its small ionic radius and low atomic number Z greatly reduce crystallographic damage of the host matrix.

The diamond host lattice

Natural diamonds have been classified into four major types based on the concentration of nitrogen and boron impurities and the lattice defects. In order of increasing rarity these are the type Ia, which has the largest amount of nitrogen (occurring in pairs at least), leading to strong absorption in the infra-red and ultra-violet. The type

Ib has less nitrogen but this is on singlet substitutional sites and is paramagnetic. The type IIa has again less nitrogen and its lattice exhibits mosaic spread. The type IIb diamond is the purest. Some of the boron acceptors are not compensated and this material is naturally p-type semi-conducting. Tables 2 and 3 of Paper 3 in the Resu and Conclusions section display these impurity concentrations.

Diamonds graphitize in high vacuum at 1800 K and their heat capacity at room temperature is about 6.2 J/gK. From this value the "melt energy" per atom is roughly 1.4 eV/atom. The activation energy for the diffusion of self interstitials is $\approx$ 1.3 eV [Pa 61], and they become mobile from room temperature. The vacancy in diamond is believed to be immobile until about 700°C [Lo 78]. The band gap is about 5.5 eV. A comprehensive review of diamond properties is to be found in reference [Fi 79].

Recoil implantation

Implanted ion doses and ranges

This section investigates the recoil implantation profile of the ^{19}F ions into diamond by the 4 MeV p^+ beam. The proton beam strikes a 30 $\mu g/cm^2$ layer of CaF_2 which is deposited onto the cleaned diamond surface by evaporation. Since the density of CaF_2 is 3.18 g/cm^2, the thickness of the probe-containing layer is typically 0.1 μm. Recoil implantation thus produces three species in the diamond target, the beam protons, the fluorine ions and the calcium ions. The implantation profiles of all these species must be evaluated in order to describe the environment of the ^{19}F probe ions.

In order to accumulate the required statistics in the TDPAD spectrum, each TDPAD experiment required about 30 hours of beam time. The averaged proton beam current on target was 5 nA, with a 6 mm diameter beam spot size. This gives an accumulated dose of implanted protons of 10^{16} ions/cm^2. Precise evaluation of recoil implantation profiles produced by this proton fluence remains an unsolved problem of physics, though there are several approximate numerical methods for evaluating it [Mo 75, Mo 76, Fi 78, Gr 81]. A simple model is presented to predict the implantation profiles of the ^{19}F recoil implanted fluorine, together with the fraction of ^{19}F that is excited to the 197 keV isomeric state, based on the schematic diagram in Fig. 2.1.

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