Optical Enhancement of NMR Signals in CdTe

by

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Abstract

Optical pumping is a powerful tool for increasing the sensitivity of NMR experiments. While it has been widely studied in GaAs, InP and other semiconductors, no previous observations have been made using direct RF inductive NMR techniques on CdTe. We have observed optically enhanced NMR signals from ^{123}Te , ^{125}Te , ^{111}Cd and ^{113}Cd in a single crystal of CdTe under excitation with near band-gap illumination. Unlike GaAs or InP, CdTe is unique in that the NMR observable isotopes naturally exist in very low abundances. This provided an opportunity to test the validity of two models describing the mechanism of optical enhancement. From a comparison of the amplitudes of the NMR signals observed from the different nuclear species, we conclude that the optical enhancement of the nuclear spin polarization in the bulk semiconductor is not consistent with a mechanism that relies on spin diffusion, but may be consistent with a recently proposed mechanism involving the direct polarization of the bulk from optically excited excitons. Optically enhanced NMR signals are observed at temperatures as high as 100 K using a tuneable 1 W laser.

Table of Contents

Abstract	ii
Table of Contents	iii
List of Tables	vi
List of Figures	vii
Acknowledgements	viii
1. Introduction	1
2. Background	3
2.1 Basic Theory	3
2.2 Spin in a magnetic field	5
2.3 Oscillating Fields	7
2.4 Oscillating fields in practice	9
2.5 Optical Pumping	10
2.6 Density matrix of photoexcited electrons	14
3. Experimental Setup	17
3.1 Sample Crystal	17
3.2 Equipment	18
3.2.1 NMR Spectrometer	18
3.2.2 Tuneable Laser	18
3.2.3 Cryostat	19
3.3 Pulse Sequence	19
3.4 Experimental Setup and Procedure	20
4. Experimental Data	21
4.1 Polarization dependence of enhancement	21
4.1.1 Polarization determination of the 1/4 wave-plate	21
4.2 Wavelength Dependence of Optically Enhanced NMR	23
4.3 Spin Species Dependence	27
4.4 Dependence on optical power	31
4.5 Temperature Dependence	32

4.6 Dependence on irradiation time and spin temperature	34
5. Conclusions and Recommendations	39
5.1 Future Direction	40
References	41
Appendices	43
Appendix A. NMR Circuit Diagrams	44
Appendix B. Signal Conditioning	46
Appendix C. CdTe Crystal Analysis	48
Appendix C.1. X-ray diffraction	48
Appendix C.2. CdTe lattice properties	49
Appendix C.3. Experimental Setup and Results	51
Appendix D. Laser usage and maintenance	53
Appendix D.1. Laser Maintenance	54
Appendix D.2. Wavelength meter	55
Appendix D.3. Optical Power Meter	55
Appendix E. Cooling the cryostat	56
Appendix E.1. Preparation of the cryostat	56
Appendix E.2. Liquid helium flow	57
Appendix E.3. Liquid Nitrogen Fill Method	58
Appendix E.4. Accurate Determination of Sample Temperature	58
Appendix F. Cernox RTD Specifications	59
Appendix G. Sample Preparation and Maintenance	62
Appendix G.1. Notes about Apiezon® N:	62
Appendix H. Spin diffusion	63
Appendix H.1. NMR Signal dependence on the diffusion constant	63
Appendix H.2. Dependence of diffusion constant on abundance	64
Appendix H.3. sim_spindiff.m	66
Appendix H.4. spindiff.m	67
Appendix I. Program Listings	69
Appendix I.1. Presat_OnePulse.x	69

Appendix I.2. Presat_OnePulse_Shutter.x 71

Appendix J. Fundamental constants and other values 73

List of Tables

Table 1 : Experimental and data processing settings for polarization variation experiments	22
Table 2 : Laser wavelength for temperature dependence measurements	33
Table 3 : Atom coordinates for CdTe unit cell	50
Table 4 : X-ray diffraction peaks for CdTe	52
Table 5 : Properties of Cernox RTD	59
Table 6 : Properties of Apiezon® Grease	62
Table 7 : Fundamental constants and other useful values	73

List of Figures

Figure 1 : NMR Pulse in practice	9
Figure 2 : Spin relaxation processes	11
Figure 3 : CdTe band structure	14
Figure 4 : CdTe transitions	15
Figure 5 : CdTe crystal	17
Figure 6 : Schematic diagram of experimental setup	20
Figure 7 : NMR signal enhancement variation with photon polarization at T= 78 K.	21
Figure 8 : NMR signal enhancement variation with photon polarization at T= 10 K	22
Figure 9 : Wavelength dependence of enhancement for ^{125}Te at 10 K.	23
Figure 10 : Wavelength dependence of enhancement for ^{125}Te, ^{111}Cd and ^{113}Cd at 78 K.	24
Figure 11 : Comparison of pre-etch and post-etch measurements for ^{125}Te, σ- polarization.	26
Figure 12 : Spin species dependence of NMR signal amplitudes.	30
Figure 13 : Laser power dependence of optically enhanced ^{125}Te NMR signal..	32
Figure 14 : Temperature dependence of optical enhancement of ^{125}Te NMR signal.	33
Figure 15 : Dependence on irradiation time for σ- polarization.	34
Figure 16 : ^{125}Te signal dependence on time τ_{light} at T = 78 K	36
Figure 17 : ^{125}Te signal dependence on time τ_{light} at T = 10 K	38
Figure 18 : NMR Circuit for ^{125}Te	44
Figure 19 : NMR Circuit for ^{123}Te	45
Figure 20 : NMR circuit for Cd	45
Figure 21 : X-ray Bragg diffraction	48
Figure 22 : CdTe unit cell	49
Figure 23 : Full x-ray diffraction spectrum	51
Figure 24 : Magnification of relevant region	52
Figure 25 : Laser calibration settings	53
Figure 26 : Numerical simulation of diffusion constant dependence on nuclear abundance.	65

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1. Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy has proven to be a powerful tool for the investigation of many materials, especially in organic samples of biological importance. However, NMR is a relatively insensitive technique, requiring large numbers of nuclei to present any observable signal. When working with biological samples, fundamental constraints placed by biology can limit the ability to arbitrarily increase the number of available nuclei, thus limiting the effectiveness of NMR in certain experimental situations.

At the same time, the production, control, and detection of spin polarization in solids, such as semiconductors, has become a topic of increasing importance for both scientific and technological applications. The use of nuclear spins in solids as qubits for quantum computation [1],[2],[3] and the emerging field of spintronics [4] are two examples where such manipulation of spin degrees of freedom are crucial.

The possibility of leveraging developments in the latter area to provide an advancement in the former is of great interest. In particular, we are interested in the ability to generate non-equilibrium nuclear spin polarization in solids by optical pumping. Such polarization has been proposed as the basis of an NMR signal enhancement technique for biological samples overlaid on semiconductor substrates [5], a technique known as transferred optically pumped NMR (TOPNMR). This technique has been proposed, but never demonstrated experimentally.

The direct inductive detection of optical polarization of nuclear spins was first performed by Lampel in Silicon [6], and has been most studied in GaAs [5]. More recently optical polarization of nuclear spins has been observed in InP [5], [7], CdS [8], and CdSe [9]. It was suggested that GaAs would not be a suitable substrate for TOPNMR because all of the abundant nuclear spin species have large quadrupolar moments that, at the surface, would interfere with polarization transfer. InP was suggested as an alternative as ^{31}P is 100% abundant, has a relatively large nuclear gyromagnetic ratio, and has spin-1/2.

CdTe is a II-VI semiconductor that has long been used in opto-electronic devices due to its favourable optical properties and near-infrared direct gap [10]. CdTe contains four spin-1/2 nuclear species in

reasonable abundance: ^{123}Te (0.91%), ^{125}Te (7.14%), ^{111}Cd (12.80%), and ^{113}Cd (12.22%), but optically-pumped nuclear spin polarization in CdTe has not, to our knowledge, been observed. As a first step, we measure the NMR properties of CdTe under optical pumping.

The process by which optically pumped nuclear spin polarization is generated is described in the literature as the result of Overhauser cross-relaxation from photo-excited electrons trapped at shallow defects [11],[12],[13],[14],[15]. In this description, nuclear spins in the bulk semiconductor are polarized by the diffusion of spin polarization from localized optical pumping sites [16], presumably defects or dopants. More recently it has been proposed [17] that polarization arising from cross-relaxation from mobile excitons may dominate the bulk polarization. The variety of isotopic abundances of the nuclear spin species in CdTe along with the dependence of the efficiency of spin diffusion with isotopic abundance provide an opportunity to test the two mechanisms.

2. Background

2.1 Basic Theory

The ability to utilize NMR as a useful spectroscopic tool depends on the difference in nuclear spin populations in the material of interest. If nuclei are placed in a static magnetic field, the nuclear spins will align either parallel or anti-parallel to the magnetic field. NMR detects the inequality between the spin populations.

For simplicity, the following discussions will assume a spin 1/2 system, where the nuclei can only assume spin $+1/2$ or $-1/2$ (spin "up" or "down", or $\uparrow$ and $\downarrow$, corresponding to the spin angular momentum vector pointing parallel or antiparallel to the static magnetic field). Further, the spins are assumed to be non-interacting.

In thermal equilibrium, the population imbalance is given by:

$$\frac{N_{\uparrow}}{N_{\downarrow}} = e^{-\frac{\gamma \hbar B_0}{kT}} \quad [1]$$

where:

$N_{\uparrow}$	=	number of nuclear spins pointing up (parallel to B_0).
$N_{\downarrow}$	=	number of nuclear spins pointing down (parallel to B_0).
γ	=	gyromagnetic ratio of the nucleus
B_0	=	magnetic field (positive for "up" direction)
T	=	temperature

To get an idea of the magnitude of numbers involved, consider the observation of protons (hydrogen) in water (e.g. for Magnetic Resonance Imaging, MRI, of the human body). A reasonable commercial MRI scanner might have a field strength with $B_0 = 2$ T. A human body is at approximately $T = 310$ K and we know $\gamma_p = 42.58$ MHz/T. Substituting in the appropriate values, one finds that:

$$\frac{N_{\uparrow}}{N_{\downarrow}} = e^{-\frac{(42.58 \times 10^6)(1.054 \times 10^{-34})(2)}{(1.38 \times 10^{-23})(310)}} = 0.9999979019 \quad [2]$$

As can be seen, the fraction observable is very small. For example, if the sample contains two million nuclei, the number of spin up and spin down nuclei will differ by just a single nucleus. In order to be able to observe an NMR signal in a reasonable amount of time, which could be measured in days, with current equipment, approximately 10^{16} nuclei are required to obtain an observable signal. Obviously, NMR is not a particularly sensitive technique.

The previous example assumes that all nuclei are potentially observable. However, this is not the case, as only nuclei with non-zero spin are observable using NMR techniques. Each element can have more than one isotope which is NMR observable, but each isotope, even for the same element, has a different gyromagnetic ratio. Therefore, in general, not all nuclei contribute to the observable signal in any single experiment. (e.g. ^{125}Te and ^{123}Te give two separate signals). Decreasing abundances of the appropriate isotope will obviously only serve to make NMR detection even more difficult. In addition to these physical limitations, consideration must be given to the spin of the nuclei. Those with spin $I = 1/2$ are generally far simpler to analyze than nuclei with spin $I > 1/2$. The number of states for a nucleus of spin I is $2I + 1$. The Zeeman splitting between each pair of adjacent states is always γB_0 , but quadrupolar couplings may change the resonant frequencies of the various transitions. Nuclei with spin $1/2$ will not have any quadrupolar couplings. In a solid material, such couplings can result in a broadened line or multiple peaks, instead of a single sharp peak. However, analysis of the quadrupolar couplings (if they exist) can provide more information about the local environment around the nuclei.

2.2 Spin in a magnetic field

The concept of nuclear spin is purely quantum mechanical. It does not exist in classical physics. However, if we consider the simplest case of spin 1/2 nuclei, the behaviour can be easily described and understood by considering the classical behaviour of a magnetic dipole moment (e.g. torque exerted on a loop of wire carrying a time-varying current) or a bar magnet. (While this description is insufficient for spins $> 1/2$, or systems of coupled spins, it can still serve as a useful starting point in understanding the behaviour of spins in a magnetic field). In the classical case, this torque τ is given by:

$$\vec{\tau} = \vec{\mu} \times \vec{B}_0 \quad [3]$$

where:

$$\begin{array}{ll} \vec{\mu} & = \text{the magnetic dipole moment} \\ \vec{B}_0 & = \text{the magnetic field} \end{array}$$

This torque will cause the dipole to align parallel with the magnetic field. If the system were completely lossless, the dipole would simply oscillate back and forth as it attempted to align with the field. For a lossy system (i.e. any real system), the oscillations would eventually decrease so that the dipole is statically aligned with the field $\vec{B}_0$.

Now consider that the dipole does not only start mis-aligned from the field $\vec{B}_0$, but that it also has angular momentum. In this case, not only will the dipole attempt to align with the field $\vec{B}_0$, it will precess while doing so. The torque and angular momentum are related by the equation:

$$\vec{\tau} = \frac{d\vec{L}}{dt}, \quad [4]$$

from which the equation for the precession can be derived. It is described by a change in the magnetic dipole moment, which can be expressed as:

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \vec{B}. \quad [5]$$

where:

$$\vec{\mu} = \gamma \vec{L}$$

Let us consider a "perfect" system, with no friction or other losses. Note that the magnitude of the change in magnetic moment is constant, and also that it is always perpendicular to both $\vec{\mu}$ and $\vec{B}_0$. This has some very interesting implications. Firstly, the rate of change in the magnetic moment is always the same for a static field. Secondly, the relative angle between $\vec{\mu}$ and $\vec{B}_0$ also cannot change. So, for a lossless system, it will precess endlessly about the magnetic field, much like a perfect, frictionless top or gyroscope. With any real, lossy system, the dipole will "spiral" in as it precesses until it eventually lines up with the field $\vec{B}_0$, but the frequency of precession does not change.

Thus far, we have been considering the situation where the observer is stationary, situated in what is usually called the laboratory frame of reference. However, it is also possible to observe from a rotating frame of reference, that is, not in the lab frame, but observing from within the frame of the experiment itself, e.g. in the frame of the dipole. In the case of a rotating frame, it can be shown that the equations of motion in the rotating frame look exactly like those in the laboratory frame, with one minor change. We first need to define an effective magnetic field:

$$\vec{B}_e = \vec{B}_0 + \frac{\Omega}{\gamma} \hat{z} \quad [6]$$

Where Ω is the angular velocity of the rotating frame. We assume that the field $\vec{B}_0$ is static and not rotating. If we observe in the rotating frame, not the static laboratory frame, the equation of motion is now:

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \vec{B}_e \quad [7]$$

Note that this is practically identical the the equation of motion for a static field, observed from the static frame. We have introduced a parameter Ω in $\vec{B}_e$, which is the rotational frequency of our rotating frame. (It arises from the derivation used to produce Equation [7], which we will not elaborate on here. More details can be found in any standard NMR textbook, such as [18]). Thus far, Ω is a free parameter, which can be chosen to be any value, whatever value we choose to be rotating at.

At this point, if we choose to observe from the rotating frame instead of the stationary frame, then the equations are just as simple and familiar as that dealing with a stationary experiment in a stationary frame. In the following sections, we will elaborate on why this will be useful.

Now, if instead of the classical derivation, one follows the quantum mechanical derivation, we can find an analogous equation:

$$\frac{d\langle\mu\rangle}{dt} = \langle\mu\rangle \times \gamma \vec{B}_e \quad [8]$$

where:

$\langle\mu\rangle$ = expectation value of the magnetic moment resulting from nuclear spin

This equation is practically identical to the classical case. In reality, one measures not a single spin, but rather the bulk magnetization of a sample which is the expectation value of the net magnetic moment of all nuclear spins in the sample.

2.3 Oscillating Fields

Here, we take a step back to remind ourselves what the detection of NMR entails (or at least RF inductive detection). The first thing that is required is a non-zero net magnetization due to nuclear spin. The second requirement is that the net magnetization be non-zero in the x - y plane (if the NMR receiver coil is aligned with its central axis on that plane). Ideally, we'd like to have the net magnetization lie completely on the x - y plane. (The main static field is, by convention, assumed to be pointing along the z -axis and oscillating fields are perpendicular, either the x -axis or the y -axis).

The first requirement suggests that we need to utilize as large a main field as possible, to enhance the population difference between the spin up and down states and thus increase the net magnetization. In order to fulfill the second requirement, we need to be able to "tip" the spins into the x - y plane. Let us first consider the case of an oscillating field in the x - y plane, which we will arbitrarily choose as a sinusoidal type field, i.e. $B_1(t) = B_1\cos(\omega t)\hat{x} + B_1\sin(\omega t)\hat{y}$ which is a field in the x - y plane rotating about the z -axis. The reason for this choice of configuration will be justified later.

In a frame rotating along with the RF, we can express the sum of the static field and oscillating as in Equation [6], and the total magnetic field is given by:

$$\vec{B}_{eff} = \left(B_0 - \frac{\omega}{\gamma}\right)\vec{k} + B_1\vec{i} \quad [9]$$

where, by usual convention, $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are unit vectors in the x , y and z directions, respectively.

The magnetization will always nutate around the effective field. However, this does not guarantee that the magnetization will ever be in the x - y plane. We need $\mathbf{B}_{\text{eff}}$ to point sufficiently away from the z -axis such that the nutation around the effective field will indeed allow the net magnetization to reach the x - y plane at some time so that a measurement can be performed. That is the $\mathbf{i}$ (chosen by convention, the $\mathbf{j}$ component will serve just as well) component of $\mathbf{B}_{\text{eff}}$ is greater than the $\mathbf{k}$ component. You can see that this is easiest if the $\mathbf{k}$ component is zero, which corresponds to $B_0 = \omega/\gamma$. This occurs when the applied B_1 is "on resonance" at the same frequency as the natural rotational frequency of the nucleus γB_0 . In this case, $\mathbf{B}_{\text{eff}}$ lies along the x -axis, about which the magnetization will nutate, so there will always be some time when it will lie in the x - y plane.

In practice, it is not necessary to be exactly on resonance but merely to be sufficiently close to resonance, (i.e. $B_0 - \omega/\gamma \ll B_1$) referring to Equation [7], so that the magnetization will be exactly in the x - y plane at some point during the precession. If we are close enough to resonance, all we have to do then is turn on the oscillating field B_1 and simply wait an appropriate amount of time. If the magnetization is initially aligned along the z -axis, the angle that the magnetization makes with the z -axis after B_1 is turned on is:

$$\theta = \frac{1}{2}\gamma B_1 t_{pw} \quad [10]$$

where:

B_1	=	strength of the perpendicular, oscillating field
t_{pw}	=	how long the oscillating field is applied for, pulse width
γ	=	gyromagnetic ratio of the nuclei

The maximum signal achievable is when $\theta = 90^\circ$, and the time t_{pw} required to do this is referred to as a 90° pulse or $\pi/2$ pulse. Obviously, if one waits twice as long (and we are exactly on resonance), the net magnetization will be pointed anti-parallel to the z -axis, and this is the 180° pulse.

If we were completely off resonance or not oscillating at all, $\mathbf{B}_{\text{eff}} = B_0\mathbf{k} + B_1\mathbf{i}$ and we would require B_1 on the order of B_0 to just be able to achieve a 90° pulse. With our first requirement for a very strong main field, this is not feasible in practice. Of course, it is much easier to simply oscillate on resonance at the Larmor frequency. This explains why we need an oscillating field, and why we have chosen a sinusoidal function.

Since each nucleus has one specific frequency, the most efficient way to accomplish this is by using a sinusoidal function which contains only the frequency of interest.

2.4 Oscillating fields in practice

How does one create a field that rotates around the z -axis in practice? One way to accomplish this is by simply using a sinusoidally oscillating field perpendicular to the z -axis. For example, using a coil oriented along the x -axis, one could generate a field whose magnitude grows and shrinks sinusoidally along the axis. Such a field can be thought of as being composed of 2 counter-rotating fields around the z -axis. One rotates at frequency ω , and the other at exactly $-\omega$. The one rotating at ω is exactly the field we want, while the one at $-\omega$ is so far off resonance that it has very little effect when it comes to tipping spins.

When one refers to a "pulse" in NMR, it is generally pictorially depicted as a simple square pulse. In practice, it is actually a sinusoidal waveform oscillating at the Larmor frequency, but modulated by a simple square pulse.

Figure 1 : NMR Pulse in practice

The actual implementation of an NMR pulse is shown above in Figure 1. The figure on the left is what is usually drawn or documented. The figure on the right shows the actual pulse sent to the NMR coil.

2.5 Optical Pumping

There are methods by which the spin population can be increased beyond the normal thermal equilibrium. One method is to take advantage of the Overhauser effect by optically pumping a sample using a source of polarized photons (i.e. laser). This method of dynamic nuclear polarization relies on the hyperfine coupling between the electron and nucleus.

In the simple picture, polarized photons of appropriate energy excite electrons into the conduction band. The polarization of the photons is transferred as spin angular momentum to the electrons. (Circularly polarized photons have a projection of the angular momentum of ± 1 on the direction of the wave vector. When photoexcitation occurs, the projection of this angular momentum is conserved by imparting it to the electron/hole pair) [19]. The photoexcitation perturbs the net spin from its thermal equilibrium distribution, so the distribution will tend to relax to the equilibrium. During this relaxation, individual electrons flip spin until the ensemble reaches the thermal equilibrium distribution. There are several mechanisms by which an electron can flip spin and lose energy. One way is via the hyperfine coupling to the nucleus, which results in enhanced nuclear polarization. However, one should keep in mind that if it were possible to observe a single electron, the probabilities of being in the spin up or down state are similar and it is possible to flip back and forth many times. What is observable using NMR is the net spin of a large ensemble of nuclear spins at some given point in time.

When optical pumping occurs in the presence of a large magnetic field, such as during NMR spectroscopy, additional effects and restrictions may come into effect. For example, if optical detection of NMR is used, a magnetic field transverse to the exciting light beam will cause the spin of the excited electrons to precess. This is observable as a change, in general a decrease, in the degree of circular polarization of the luminescence resulting from the recombination of excited electrons. This is known as the Hanle effect, and was discovered in 1924 [20]. In the case of "standard" RF inductive NMR, the electron spin precession caused by the transverse tipping field could affect the degree of nuclear spin polarization enhancement occurring via the contact hyperfine coupling between the nucleus and electron.

Note that Overhauser cross-relaxation is not the only way for the electrons to relax. There are several other electron spin relaxation processes which do not result in enhanced nuclear polarization [21]. The Elliot-Yafet mechanism results from spin-orbit interactions in crystals. This interaction allows electron

wave functions with opposite spins to mix so that while the spin angular momentum is conserved for the sum of the mixed electrons, it is possible for the spin of each individual electron to become depolarized. The D'yakonov-Perel mechanism arises from effective internal magnetic fields caused by spin splitting of the conduction band states. If the Larmor frequency is very much smaller than the frequency of momentum scattering events, the electron spin relaxes via small rotations during each scattering event. Electron scattering from holes (such as via the Bir-Aronov-Pikus mechanism) can also cause electron spin flips, which would obviously not be transferred to the nucleus. In order for optical pumping to produce a substantial enhancement of the nuclear spin polarization, relaxation through the hyperfine coupling must be sufficiently probable compared to these other effects, which is why optical pumping is not usually viable at room temperature.

Also recall that the nucleus itself can have a reasonable probability of relaxing in a short amount of time. This is simply via the normal spin-lattice relaxation process. If this process occurs too quickly, any nuclear spin population enhancement will not be detectable.

Figure 2 : Spin relaxation processes

Figure 2 shows a simple diagram of the various processes affecting spin polarization. Using photons of appropriate polarization and energy, it is possible to generate electron spin polarization. For the electron spin relaxation, we are only interested in the electron-nucleus contact hyperfine coupling. There are other possible couplings between electron spin and nuclear spin, but these are generally negligible in this case, and so will not be considered. Nuclear spin relaxation to the lattice will tend to de-polarize the nuclear

spins. In order to be able to observe the effects of optical pumping, we require that $(T_1)_n$ be much longer than the time scale for the electron-nucleus contact hyperfine coupling.

The Hamiltonian which describes the scalar contact hyperfine coupling between the electron and nucleus is given by:

$$H = -\frac{8\pi}{3}\gamma_e\gamma_n\hbar\delta(r_I)(\mathbf{I} \cdot \mathbf{S}) \quad [11]$$

where:

- $\mathbf{I}$ = the nuclear spin
- $\mathbf{S}$ = the electron spin
- γ_n = gyromagnetic ratio of the nucleus
- γ_e = gyromagnetic ratio of the electron
- r_I = position of the electron relative to the nucleus, and $\delta(r_I)$ is just the Dirac δ -function.

We are neglecting any contributions from dipolar and orbital hyperfine couplings, because the effects caused by these other couplings will not be observable in our experiments. The dipolar coupling would cause an anisotropy of the Knight shift [22], and the orbital part will cause a shift of the electronic g -factor different from its theoretical value calculated from spin only.

The relaxation rate of the nuclear spins due to contact hyperfine coupling [22] is given approximately by:

$$\left(\frac{1}{T_1}\right)_{n_e_ch} \propto \frac{64\pi^3}{9}\gamma_e^2\gamma_n^2\hbar^3|\psi_F(0)|^4\tau_c N_e \quad [12]$$

where:

- τ_c = the correlation time of the electrons
- $|\psi_F(0)|^2$ = the wave-function density of the electron at the nucleus
- N_e = the effective number density of the electrons, accounting for Pauli exclusion

While the above equation was originally derived under the assumption that the nuclear spins are 1/2 and that the applied magnetic field is sufficiently high, it can be shown that the equations apply in general to an arbitrary magnetic field and to any system of nuclear spins. The only requirement being the existence of a spin temperature.

Now we consider the situation of nuclear polarization by contact hyperfine coupling to the electrons. The first such experiments were performed as dynamic nuclear polarization (DNP) experiments, where the electron spin system was disturbed from thermal equilibrium by irradiation with an on-resonant (for the electrons) radio-frequency or microwave field. In that case, the maximum possible enhancement of the NMR signal is given by [22]:

$$A = \frac{\langle I_z \rangle}{I_0} = \left(1 - fs \frac{\gamma_e}{\gamma_n} \right) \approx fs \left| \frac{\gamma_e}{\gamma_n} \right| \quad [13]$$

where:

- I_0 = thermal equilibrium value of the total spin
- $\langle I_z \rangle$ = expectation value of the total spin after dynamic nuclear polarization
- f = factor which accounts for the relative rate of nuclear polarization from the hyperfine contact coupling to the electron.
i.e. $f = r(\text{hyperfine_contact}) / [r(\text{hyperfine_contact}) + r(\text{other})]$, where r is the relative rate of nuclear spin relaxation from all processes. In the ideal case, the hyperfine contact coupling is the only nuclear spin relaxation processes and $f = 1$.
- s = factor to account for incomplete saturation of electron spin polarization.
For complete saturation, $s = 1$.

This formalism applies to the optical pumping case as well, where s describes the spin polarization of the electrons in quasi-equilibrium, and is given by:

$$s = \frac{S_0 - \langle S_z \rangle}{S_0} \quad [14]$$

where:

- S_0 = the equilibrium electron polarization
- $\langle S_z \rangle$ = is the expectation value of the spin for one electron.

The approximation used in Equation [13] holds true if the ratio of $\gamma_e/\gamma_n \gg 1$, which is typically the case. For ^{125}Te nuclei, $\gamma_e/\gamma_n = 658.21/0.31549 = 2086$. In practice, it is usually not possible to achieve this value of NMR signal due to relaxation of the electron and nuclear spins.

The factor f represents the fraction of nuclear relaxation processes which are due to contact hyperfine coupling to the electron which can produce the dynamic nuclear polarization.

$$f = \frac{\left(\frac{1}{T_1}\right)_{n_{e_ch}}}{\left(\frac{1}{T_1}\right)_{n_{e_ch}} + \left(\frac{1}{T_1}\right)_{n_{other}}} \quad [15]$$

where:

- $(1/T_1)_{n_{e_ch}}$ = corresponds to the time for nuclear spin relaxation via hyperfine contact coupling with the electron
- $(1/T_1)_{n_{other}}$ = corresponds to the time for all other nuclear spin relaxation processes

In the case of our CdTe sample, the thermal equilibrium nuclear relaxation time is very long at low temperatures (on the order of 10^4 s). Other than the spin-flips caused by electron-nucleus hyperfine interactions, there are approximately no other nuclear spin relaxation processes during the time scales of our experiment. Therefore, we can make the assumption that $f \sim 1$.

2.6 Density matrix of photoexcited electrons

Figure 3 : CdTe band structure

CdTe is a direct-bandgap II-VI semiconductor. The band structure schematic near the Γ point in zero field is shown in Figure 3. The bandgap is temperature dependent. E_g is on the order of 1.53 eV, and the separation to the split-off band Δ is around 0.9 eV. The $P_{3/2}$ valence band is degenerate at the bandgap, and has one band for heavy holes and one for light holes. At the bandgap, the heavy-hole transition occurs with 3 times the probability of a light-hole transition. Because of the relatively large separation to the split-off band, transitions from this band are neglected for the purposes of this experiment.

The possible transitions due to left (σ^-) and right (σ^+) circularly polarized photo-excitation are shown below in Figure 4.

Figure 4 : CdTe transitions

The laser used for this experiment does not have sufficient energy to excite the transitions from the $P_{1/2}$ band to the $S_{1/2}$ conduction band, so we are primarily concerned with the heavy hole transitions from the $P_{3/2}$ band.

The quantity of interest is the expected spin of an electron at the instant of creation. It can be shown that for heavy hole transitions [19]:

$$\mathbf{S}_{op}(\nu) = -\frac{\nu(\nu \cdot \mathbf{n})}{1 + (\nu \cdot \mathbf{n})^2} \quad [16]$$

For a first approximation, we will ignore the light hole transitions for the reasons noted previously, however, for completeness, we note that for light-hole transitions, the expected spin of an electron is given by:

$$\mathbf{S}_{op}(\nu) = \frac{3\nu(\nu \cdot \mathbf{n}) - 2\mathbf{n}}{5 - 3(\nu \cdot \mathbf{n})^2} \quad [17]$$

where:

$\mathbf{S}_{op}$	=	the expected spin of a conduction band electron at the instant of creation, in the direction of the electron momentum ν .
ν	=	unit vector in the direction of the electron momentum
$\mathbf{n}$	=	unit vector along the direction of the exciting photon beam

In the case of high-resistivity undoped CdTe, unlike in a metal for example, only photoexcited electrons exist in the conduction band. The expected spin of the conduction band electron shortly after creation (i.e. at some time less than the spin lifetime), S , is different from that of S_{op} due to spin relaxation processes. Obviously, if electron spin relaxation never occurred, $S = S_{op}$. The relationship is given by:

$$S(\nu) = \frac{S_{op}(\nu)}{1 + \frac{\tau}{T_{1e}}} \quad [18]$$

where:

$$\begin{array}{ll} \tau & = \text{electron (exciton) lifetime} \\ T_{1e} & = \text{electron spin relaxation time} \end{array}$$

In conjunction with Equation [14], this can provide an estimate of the factor s , which can help to predict the maximum possible enhancement from optical pumping. In order to do this, we will need to obtain accurate values of the lifetime and spin relaxation time. Unfortunately, at the current time, there is a lack of published data on undoped, high-resistivity CdTe samples at low temperatures. The electron carrier recombination lifetime in high-resistivity intrinsic CdTe (compensated with In) has been measured to be on the order of 100 ps [23] at room temperature. But of course it is not immediately obvious that this is directly applicable to a high-resistivity intrinsic CdTe sample which is not compensated. Carrier relaxation processes have also been measured in bulk un-doped CdTe [24], with those being attributed to spin-relaxation on the order of 2 ps at 290 K. However, accurate extrapolation of room temperature data to 78 K and 10 K is not trivial.

3. Experimental Setup

3.1 Sample Crystal

All measurements were performed on a single undoped crystal of CdTe measuring 2.1 mm × 4.8 mm × 1.1 mm (obtained from University Wafer, South Boston, MA, USA, Lot No. 6796). The resistivity of the sample was specified by the manufacturer to be $10^9 \Omega\cdot\text{cm}$.

Figure 5 : CdTe crystal

The crystal is not tough, so care should be taken during handling. The largest faces have been polished by the manufacturer already. Other experiments were performed on the crystal to attempt to determine more of the sample characteristics and these are detailed in Appendix C.

Based on crystals of similar resistivity [25],[26] we estimate that the carrier concentration is $6 \times 10^6 / \text{cm}^3$ or less. This is based on the assumption that the majority carriers are electrons, which have a mobility of $\sim 1000 \text{ cm}^2/\text{V}\cdot\text{s}$. The carrier concentration at room temperature (assuming all potential donors are ionized) can be approximately calculated using the following relation:

$$N_D = \frac{1}{\mu_e R q} \quad [19]$$

where:

N_D	=	carrier (electron) concentration [cm^{-3}]
μ_e	=	carrier (electron) mobility [$\text{cm}^2/\text{V}\cdot\text{s}$]
R	=	resistivity [$\Omega\cdot\text{cm}$]
q	=	carrier charge [C], normally $1.6 \times 10^{-19} \text{ C}$.

The same analysis can be performed if the majority carriers are holes. However, in this case, the mobilities are approximately an order of magnitude lower, $\mu_h \sim 80 \text{ cm}^2/\text{V}\cdot\text{s}$.

3.2 Equipment

3.2.1 NMR Spectrometer

Experiments were carried out in an 8.433 T magnet from Oxford Instruments using a homebuilt NMR spectrometer [27] and Janis Research (Supertran) continuous flow cryostat that had been fitted with the rotary motion feedthroughs, coaxial cables and cryogenic capacitors required for operation as a low temperature NMR probe. The CdTe crystal was mounted on a piece of Al_2O_3 (sapphire) to provide thermal contact to the probe's cold-finger while maintaining electrical insulation. Grooves were cut into the Al_2O_3 substrate to allow the NMR coil to encircle the sample. The sample temperature was controlled with a Lakeshore Model 340 temperature controller (Lakeshore Cryotronics, Westerville, OH, USA) that monitored a Cernox RTD (Lakeshore) mounted inside the cold-finger. See Figure 6 for a diagram of the experimental setup.

3.2.2 Tuneable Laser

A 1 W tuneable Ti:Sapphire laser (899-LC, Coherent Inc, Santa Clara, CA, USA) was used for optical excitations. This laser is capable of operating in several wavelength regions, which is accomplished by installing the appropriate optic element (output coupler), which is supplied with the laser. Three different output couplers are available, one each for short wavelength (SW) use, medium wavelength (MW) and long wavelength (LW). Appendix D. contains some more details about the capabilities of the laser when used with the different output couplers. The SW element was used for all experiments. Laser output power and wavelength were measured at the source with a Coherent Fieldmaster GS power meter and a Coherent Wavemate wavelength meter. A series of mirrors were used to steer the beam through a zero-order $1/4$ wave plate and two clear quartz windows and onto the sample as shown in Fig. 1. The beam diameter at the target was approximately 5 mm. Optical loss after the three mirrors was measured to be less than 1%.

A spectrometer controlled shutter provided control of the irradiation time. All spectra, except as noted, were acquired following 10 s of dark time so that the electron system could return to the ground state. No change in the signal amplitude or lineshape was observed if the sample remained irradiated during acquisition. This is consistent with similar measurements on GaAs using a similar setup [17].

The sample temperature increase due to laser heating was estimated, with 300 mW laser output, to be less than 2 K during a complete acquisition cycle, even without dark time. This was determined by placing a

second Cernox RTD (Lakeshore) inside the cryostat immediately adjacent to the CdTe crystal on the same piece of Al₂O₃. The RTD was covered with PTFE (Teflon®) tape to avoid exposure to laser light.

3.2.3 Cryostat

The Janis Research (Supertran) cryostat was previously modified by Matt Grinder [28].

The cryostat is of continuous flow type, and is designed to utilize either liquid helium or nitrogen flowing through the cryostat to provide the necessary cooling. The original radiation shield was fitted with a custom quartz window from Janis. This is designed to cover the sample area, within the original probe casing, which also has a quartz window at the bottom.

3.3 Pulse Sequence

The pulse sequence used for acquisition of the NMR signals was:

$$\text{SAT} - \tau_{\text{light}} - \tau_{\text{dark}} - \text{ACQ}$$

where:

SAT	=	pre-saturation sequence, a sequence of 50 90° pulses separated by 1 ms.
τ_{light}	=	120 s
τ_{dark}	=	10 s, except where noted
ACQ	=	the acquisition of the free induction decay following a 90° pulse.

Signals were averaged over 4 identical acquisition sequences, except where noted. The pulse width used for a 90° tip angle was 6 μ s with output power of approximately 316 W. This measurement was performed on the coil and circuit used for the ¹²⁵Te measurements. The resonance peak of the circuit for ¹²⁵Te and for both the Cd nuclei were measured using an oscilloscope and a frequency sweep generator. The resonance peak width was indistinguishable at each of the frequencies used, so we expect similar RF performance. The circuits used are detailed in Appendix A.

3.4 Experimental Setup and Procedure

The optical power meter was inserted into the beam line just prior to data acquisition to confirm the power settings, and removed from the optical path prior to initiating the experiment.

Figure 6 : Schematic diagram of experimental setup

4. Experimental Data

4.1 Polarization dependence of enhancement

One piece of evidence which helps to determine if the enhancement of NMR signal is due to optical pumping, is its behaviour at various light polarization angles. Data was collected while varying the angle of the 1/4 wave-plate, effectively rotating the photon polarization. Enhancement due to the heating effects of the laser should not show any systematic variation with polarization angle. Conversely, any signal enhancement due to optical pumping with polarized light should show a sinusoidal variation.

4.1.1 Polarization determination of the 1/4 wave-plate

A notch on the 1/4 wave-plate denotes the slow axis. When aligned to 0° , the 45° setting corresponds to σ^+ and 135° corresponds to σ^- for incident light from the laser which is linearly polarized along the slow axis of the 1/4 wave-plate.

Figure 7 : NMR signal enhancement variation with photon polarization at $T = 78$ K.

Figure 7 shows the results at $T = 78$ K. (The solid curve is a least-squares fit to the data). The variation with photon polarization is as expected for optical pumping, however, it is unusual in that the signal never

inverts (i.e. less than zero). Measurements at a lower temperature ($T = 11$ K) were taken with a similar setup, but over a reduced range of photon polarizations. The results are shown in Figure 8. (The results are very poor and shown for completeness only. They should not be used for any quantitative analysis. The measurements at $T = 78$ K are sufficient data for the purposes of this experiment).

Figure 8 : NMR Signal enhancement variation with photon polarization at $T = 10$ K
The integrated signal refers to the total area of the NMR peak signal, not the peak maximum. Also of note, the offset of the signal is not due to the noise floor. The minimum signal visible at $\sigma+$ polarization is greater than that of the non-optically pumped signal.

Table 1 : Experimental and data processing settings for polarization variation experiments

Parameter	$T = 78$ K	$T = 11$ K	Unit
Left shift (referenced to 1st data point)	33	50	points
Exponential Multiply	200	200	-
Laser	300	150	mW
Wavelength	800	800	nm
Hardware Attenuation	25	25	dB
Pulse Width	6	6	μ s
Temperature	78.5	11	K
Temperature Control Method	Liquid N ₂ fill	He flow	

4.2 Wavelength Dependence of Optically Enhanced NMR

The wavelength dependence of the optically enhanced ^{125}Te NMR signal at 10 K is shown in Figure 9. Without optical pumping, there is no visible NMR signal under the same conditions. The peak in the observed enhancement occurs very close to the bandgap of CdTe, given in eV by [29]:

$$E_g(T) = 1.56 - 4.1 \times 10^{-4}T \quad [20]$$

which at 10 K corresponds to approximately 1.55 eV (797 nm).

Figure 9 : Wavelength dependence of enhancement for ^{125}Te at 10 K. The insets show a bandwidth of ~ 40 kHz, and the FWHM of the signal is approximately 1.5 kHz.

The arrow labelled E_g corresponds to the approximate value of the bandgap in the cubic (zincblende) form of CdTe. The 2 smaller arrows indicate the approximate bandgaps of the hexagonal (wurtzite) form of CdTe, based on experimental results at 2 K [30].

Measurements of the optically enhanced NMR signals acquired from ^{125}Te , ^{111}Cd , and ^{113}Cd at 78 K are shown in Figure 10 .

Figure 10 : Wavelength dependence of enhancement for ^{125}Te , ^{111}Cd and ^{113}Cd at $T = 78\text{ K}$

The peak in enhancement for σ^- polarized light is again in agreement with the bandgap of CdTe at 78 K, which is calculated from Equation [20] to be 1.53 eV (810 nm).

The largest NMR enhancements are observed with σ^- irradiation and are absorptive. This is consistent with the negative electronic g -factor [31] and negative gyromagnetic ratio for all four nuclear spin species (the static field, B_0 , in our magnet points down).

We expect the sign of the nuclear spin polarization to invert as the excitation is changed from σ^- to σ^+ . However, no such inversion occurs and the signals are always absorptive. This lack of inversion has also been observed in a Be-doped GaAs sample [14] and was attributed to the efficiency of electron-spin relaxation or a large difference in recombination rates between spin up and down photoelectrons.

Two minor peaks in the NMR signals are visible in some curves of Figure 9 and Figure 10 at photon energies above the bandgap. There are various possible explanations for additional peaks in the spectra. Excitation to the next higher conduction band levels requires energies that are several eV higher [32]. The gap between the fundamental free exciton level and the first excited state of the free exciton is approximately 7.5 meV [33] [34], which is too small to explain the features seen in the spectra. Additional

peaks could be attributed to surface phonon modes [35], or spaced by the LO phonon energy [36]. However the spacing between the features we observe and the bandgap too large to be explained by surface phonon modes and too large to be explained by the 21 meV [37] of LO phonons in CdTe. The $P_{1/2}$ split off band is approximately 0.9 eV ($[\Gamma_7^v - \Gamma_6^c]$) higher in energy [24] corresponding to approximately 510 nm, and is out of the range of excitation energies accessible with our laser.

One possibility is that these two peaks are due to the existence of a Wurtzite (hexagonal) phase in, or at the surface of, the crystal. The energy of these two peaks show good correspondence to photoluminescence measurements on the bandgap of CdTe in the Wurtzite phase [30], which also shows two peaks ($[\Gamma_9^v - \Gamma_7^c]$ and $[\Gamma_7^v - \Gamma_7^c]$) with similar energy separation. In II-VI semiconductor materials, the $\pm\{111\}$ facet of the Zincblende phase and the $\pm(0001)$ facet of the Wurtzite phase are atomically matched. The existence of multiple phases in a single crystal (polytypism), has been observed in several types of semiconductors [38],[39],[40],[41],[42] and specifically, has been shown to occur in CdTe [43], depending on the crystal growth conditions. Relatively small changes in temperature and other conditions during crystal growth can be sufficient to induce polytypism and this has recently been exploited to control the manufacture of polytypic CdTe crystals [44].

After all other measurements were complete, one surface (the one exposed to the laser in all prior data), was etched in HCl for approximately 10 minutes. The crystal was then rinsed and submerged in de-ionized water before being immediately placed back into the cryostat and pumped out.

Measurement of optically pumped ^{125}Te NMR signal at $T = 78\text{ K}$ were repeated with the σ - polarization, with the wavelength varied from 740 nm to 810 nm. Optical power was set to 400 mW. The data was normalized to the primary peak and compared to the pre-etch data.

Figure 11 : Comparison of pre-etch and post-etch measurements for ^{125}Te , σ - polarization.

As can be seen in Figure 11, the secondary peak is reduced to approximately 60% the size of the pre-etch data. While this does not prove the existence of a wurtzite phase, it is suggestive that a (removeable) surface feature is responsible for the secondary peaks in the spectrum.

4.3 Spin Species Dependence

A key feature of a recently proposed mechanism for the optical polarization of nuclear spins in the bulk [17] is that it does not involve the transport of nuclear spin polarization by spin diffusion. This is in contrast to the previous description of such bulk polarization [11][15]. Measurement of the optically pumped nuclear spin polarization for the various NMR active isotopes in CdTe allows a comparison with predictions based on each of these models. We begin with a calculation of the relative signal amplitudes expected from the different spin species for the two mechanisms.

In the newly proposed mechanism [17], nuclear spins in the bulk semiconductor are directly polarized by contact hyperfine coupling to mobile excitons. The magnitude of this coupling can be expressed as [45]:

$$A_{hf} = \frac{8\pi}{3} \gamma_n \gamma_e \hbar^2 |\psi(0)|^2 \quad [21]$$

where:

γ_n	=	gyromagnetic ratio of the nucleus.
γ_e	=	gyromagnetic ratio of the electron
$ \psi(0) ^2$	=	wave-function density of the electron at the nucleus of interest.

The relaxation rate is proportional to A_{hf}^2 [46], and the observed signal will also be proportional to the abundance A of the nuclear spin species, as well as an additional factor γ_n to account for the increased signal observed at higher resonance frequencies. We thus expect the amplitude of the detected NMR signal to be given by:

$$S \propto \gamma_n^3 A |\psi(0)|^4 \quad [22]$$

where we have dropped factors that are common for all of the different nuclear spin species.

Equation [22] accounts for the increased signal intensity at higher resonance frequencies, which is $\propto \gamma$, but does not account for the degradation of the NMR coil quality factor (i.e. the Q of the circuit). An experimental dependence of $\gamma^{0.5}$ is usually used [47] to account for this.

However, in this experiment, the same NMR coil was used for all measurements, the only change being the capacitors used to set the resonance frequency. We calculate that the expected deviation in circuit quality

[47] between ^{125}Te and the two Cd species is less than 10%. This estimate was verified experimentally by using a frequency sweep generator and observing the width of the resonant peak for each circuit configuration. There is no significantly observable difference between the configurations used for ^{125}Te and the two Cd species.

In the case where the bulk semiconductor is polarized by nuclear spin diffusion from fixed sites (e.g. point defects), we expect, for our illumination time of 120 s, that a small region around each fixed site will be in quasi-equilibrium, where [48]:

$$\frac{1}{T_n} = \mp \frac{\gamma_e}{\gamma_n} \left(\frac{1}{T_e} - \frac{1}{T} \right) \quad [23]$$

where:

$$\begin{array}{lll} T_n & = & \text{nuclear spin temperature} \\ T_e & = & \text{electron spin temperature} \\ T & = & \text{lattice temperature} \end{array}$$

the upper sign should be taken if the electron g factor and nuclear γ have the same sign. In this quasi-equilibrium the fractional polarization of all spin species in some core region around the fixed site, proportional to γ_n/T_n is equal. The rate of diffusion of spin polarization from this core region then depends upon the abundance of the nuclear spin species as well as on γ_n .

For a fixed lattice geometry, the spin diffusion coefficient D can be written:

$$D = c \frac{\gamma^2}{r} \quad [24]$$

where:

$$\begin{array}{lll} c & = & \text{a constant of order unity} \\ r & = & \text{nearest neighbour distance} \end{array}$$

A mean-field treatment for a diluted lattice would then lead to the expectation that $D \propto \gamma_n^2 A^{1/3}$. At low abundance, D should fall below the mean-field value as polarization gets trapped in clusters of nearby spins, as accounted for by including exponential cut-offs [49] or nearest-neighbour restrictions [50] in numerical simulations of spin diffusion.

In the regime where neighbouring polarization sources are far apart compared to $(Dt)^{1/2}$, the total spin polarization in the region surrounding a single pumping site is proportional to D , and, adopting the mean-field prediction for D , we expect the signal to be given by:

$$S \propto \left(\gamma_N^2 A^{\frac{1}{3}} \right) \gamma_N A \quad [25]$$

We should note that on first glance, Equation [25] above and the one for the mobile exciton model, Equation [22] do not appear to be consistent in their units of measure. Both proportionality equations depend on γ^3 . A represents the nuclear abundance and has no unit. The $|\psi(0)|^4$ factor from Equation [22] has units of inverse volume squared, but from the detailed derivation by Bloembergen [46], the signal strength is also proportional to the square of the unit cell volume, cancelling out the contribution from $|\psi(0)|^4$. Hence, the units in both models are consistent. The factor involving the unit cell volume size has not been included in Equation [22] because the unit cell is the same size for all species (all nuclei are residing in the same crystal lattice), and thus do not play a part when comparing relative signal strengths between the nuclei.

A comparison of the NMR signals observed from all four nuclear spin species with the predictions of these two mechanisms is shown in Fig. 4. Values of $|\psi(0)|^2$ used are those calculated using localized orbital methods [51] (0.4 for Te and 0.22 for Cd).

The spin diffusion coefficient will be modified from the mean-field prediction by the clustering effect noted above and also by the suppression of diffusion by couplings to neighbouring spins of different γ [52]. We take the ^{125}Te signal as a baseline and compare the abundance and environment of the other nuclear species to it. The two Cd isotopes have similar γ , similar abundance, and similar environment with respect to the density and gyromagnetic ratios of neighbours. Because the Cd isotopes are the most abundant and have the fewest neighbours with nuclear spins, we expect that compared to the Te species, their diffusion coefficients will be least affected by both of the two effects described. ^{123}Te , on the other hand, is the least abundant, and has the largest number of neighbours with nuclear spins, and so it should be affected the most by both effects. These predictions are represented by the arrows in Figure 12. They show that the model

incorporating spin diffusion can only fit the data even more poorly if spin diffusion effects are taken into account.

Figure 12 : Spin species dependence of NMR signal amplitudes (using σ - polarization optical excitation). Expected intensity is based on the mobile exciton model. Arrows show how data points would shift in the case of the model assuming spin diffusion from fixed sites.

The model describing polarization of the bulk directly from excitons provides a much better fit to the data. A linear regression based on Equation [25] provides $R^2 = 0.86$, while a similar regression based on Equation [22] found $R^2 = 0.60$, providing strong evidence that the polarization of the bulk semiconductor does not depend on nuclear spin polarization from fixed pumping sites.

4.4 Dependence on optical power

The dependence of the amplitude of the NMR signal acquired as a function of the incident laser power is shown in Figure 13.

The dependence of the signal amplitude on optical power has been predicted [5] to be:

$$S(P_{in}) = S_{max} \int_0^{z_d} \left[1 - e^{\left(-\frac{P_{in} e^{-\frac{z}{z_0}}}{P_s} \right)} \right] dz + S_{bulk} \quad [26]$$

where:

z_0	=	the absorption depth in the sample (wavelength dependent but is $\sim 1.15 \mu\text{m}$ [53]) for the wavelengths used in this experiment).
z_d	=	the thickness of the sample
P_{in}	=	the incident optical power density
P_s	=	the saturation power density
S_{bulk}	=	the signal arising from thermal relaxation in the bulk semiconductor substrate below the optically pumped layer
S_{max}	=	is the signal expected from the optically pumped layer if fully polarized.

This equation does not include contributions from photobleaching, reabsorption of luminescence or differential absorption of different light polarization states. Note that the development of this equation assumes that the signal amplitude is the NMR signal amplitude with optical excitation at a single fixed polarization. (i.e. the signal $S(P_{in})$ is not $|S(\sigma+) - S(\sigma-)|$).

Figure 13 : Laser power (σ - polarization) dependence of optically enhanced ^{125}Te NMR signal

A fit of Equation [26] to the data, assuming $S_{\text{bulk}} = 0$ and $z_d = \infty$, yields a saturation power $P_s \approx 230 \text{ mW/cm}^2$, somewhat higher than the $60 - 123 \text{ mW/cm}^2$ observed in InP [5] and GaAs [54].

4.5 Temperature Dependence

The enhancement of the NMR signal due to optical pumping is expected to decrease rapidly with increasing temperature as other pathways for electron spin relaxation become faster relative to the contact hyperfine coupling with the nucleus. The nuclear spin relaxation time also decreases with increasing temperature. In other materials, this can render any potential optical pumping effect difficult to observe if the relaxation time is sufficiently short, as any enhanced spin population quickly relaxes back to its thermal equilibrium distribution. However, for this CdTe sample, this is not of concern as the room temperature T_1 is on the order of 1000 s.

Figure 14 : Temperature dependence of optical enhancement of ^{125}Te NMR signal. Optical power is 500 mW

Figure 14 shows the behaviour of the ^{125}Te NMR optically pumped signal over a temperature range of 10 K up to 100 K. As expected, the optical enhancement diminishes rapidly as the temperature is raised, however, we are able to observe an enhancement in signal above 100 K in both ^{125}Te and ^{111}Cd with the laser tuned to 600 mW at 800 nm. The optical energy was varied to match the theoretical bandgap based on Equation [20]. The settings for each datapoint are listed below in Table 2. Note again that the signal does not correct for the base signal level which results from the non-optically enhanced signal.

Table 2 : Laser wavelength for temperature dependence measurements

Temperature [K]	Theoretical Bandgap [nm]	Laser Wavelength [nm]
10	796.87	796.9
15	797.92	797.9
25	800.03	800.0
40	803.21	803.2
60	807.50	807.5
75	810.75	810.7
100	816.22	816.2

4.6 Dependence on irradiation time and spin temperature

Measurements of polarization enhancement dependence on irradiation time were performed on ^{125}Te and ^{111}Cd using a single polarization of light (σ^-), except where noted. The pulse and acquisition sequence is the same as previously described:

$$\text{SAT} - \tau_{\text{light}} - \tau_{\text{dark}} - \text{ACQ}$$

with the exception that τ_{light} is varied between 10 s and 120 s. The experimental setup for all nuclei are identical (except for the NMR coil circuit, refer to Appendix A. for more details).

Figure 15 : Dependence on irradiation time for σ^- polarization. The grey line denotes the approximate noise level

The result measuring dependence on irradiation time is shown in Figure 15. The level of the contribution from the base non-optically enhanced signal is denoted by the horizontal line above the axis, but this value has not been subtracted from the plotted data points. The signals at very low irradiation times are almost non-existent and difficult to distinguish from the noise, as expected. ^{125}Te signal enhancement appears to increase at a much faster rate than that from ^{111}Cd . However, both appear approximately linear and no saturation limit has been reached at 120 s.

In order to estimate the total nuclear spin polarization that could be excited, the amplitude of the maximum NMR signal following a long period of optical excitation was compared to reference spectra acquired from the same sample in thermal equilibrium at room temperature. The acquisition sequence used is the same as described previously, except that the laser is allowed to be continuously on (i.e. $\tau_{\text{dark}} = 0$), using 500 mW of optical power.

To provide for a meaningful comparison, the same experimental setup conditions were used at both temperatures. However, the laser irradiation times used at both temperatures differed slightly (2400 s for $T = 78$ K and 2500 s for $T = 10$ K). This difference was not intentional.

The received NMR signal is proportional to the difference in populations between the spin up and spin down populations.

$$S = C \frac{N_{\downarrow} - N_{\uparrow}}{N_{\downarrow} + N_{\uparrow}} = Cp \quad [27]$$

where:

S = NMR signal strength, and is implicitly dependent on the temperature T .
C = some unknown constant which is dependent on the overall spectrometer gain.

From Equation [2], we can write:

$$N_{\uparrow} = N_{\downarrow} e^{-\frac{\gamma \hbar B_0}{kT}} \quad [28]$$

Substituting [28] into [27], we can then write:

$$S(T) = C \frac{N_{\downarrow} - N_{\downarrow} e^{-\frac{\gamma \hbar B_0}{kT}}}{N_{\downarrow} + N_{\downarrow} e^{-\frac{\gamma \hbar B_0}{kT}}} = C \frac{N_{\downarrow} \left(1 - e^{-\frac{\gamma \hbar B_0}{kT}}\right)}{N_{\downarrow} \left(1 + e^{-\frac{\gamma \hbar B_0}{kT}}\right)} = C \frac{\left(1 - e^{-\frac{\gamma \hbar B_0}{kT}}\right)}{\left(1 + e^{-\frac{\gamma \hbar B_0}{kT}}\right)} \quad [29]$$

This expression can be made slightly simpler by multiplying both the denominator and numerator by $e^{+\frac{\gamma \hbar B_0}{2kT}}$ (e.g. effectively multiplying by 1), and making use of some hyperbolic identities, we can re-express as:

$$S(T) = C \tanh\left(\frac{\gamma \hbar B_0}{2kT}\right) \quad [30]$$

At this point, there is still the matter of C , an unknown value. This can be eliminated if we have a measurement at thermal equilibrium at a known temperature, which we conveniently choose to be room temperature ($T = 290$ K). A more useful expression is then:

$$\frac{S(T)}{S(290)} = \frac{\tanh\left(\frac{\gamma \hbar B_0}{2kT}\right)}{\tanh\left(\frac{\gamma \hbar B_0}{2k(290)}\right)} \quad [31]$$

From Equation [31], all values are known except for the temperature T . This temperature is not known during optical pumping because the system is not in thermal equilibrium with the lattice. In this case, T represents the effective nuclear spin temperature which will be denoted as T_n .

Figure 16 : ^{125}Te signal dependence on time τ_{light} at $T = 78$ K. Polarization is σ^- .

Integrated signal shown refers to the total NMR peak signal area for a given acquisition, not the maximum value of the peak.

At 78 K, the ^{125}Te NMR signal displayed an approximately exponential time dependence on τ_{light} , where $\tau_{\text{light}} = \tau$ is the time delay between successive measurements in a saturation recovery experiment. (i.e. sample was continuously illuminated between acquisitions). The estimated relaxation time is ~ 1000 s

based on the best fit (least squares minimum) curve to the data, shown in Figure 16. In the absence of optical excitation, the ^{125}Te T1 at 78 K is > 10000 s. Several data points were taken without optical enhancement and one can see in Figure 16 the size of this signal relative to the optically enhanced signal.

From these measurements, the data point at $\tau = 2400$ s was selected for comparison to a reference signal taken at 290 K in thermal equilibrium, which was acquired using the same experimental setup. The ratio of the optically-pumped signal at 78 K to the thermal equilibrium signal at 290 K was approximately 6.7, i.e. $S_{\text{measured}}(78) / S_{\text{measured}}(290) = 18.75/2.75 = 6.7$.

The number of nuclei contributing to the optically pumped signal is not the same as that contributing to the measurement at thermal equilibrium. When the sample is in thermal equilibrium, the nuclei from the entire crystal volume contributes to the signal. At 78 K, the volume of the crystal which is not optically pumped is assumed to contribute negligibly to the NMR signal. Thus, the relevant number of nuclei is contained only in the volume of crystal which is optically pumped.

The optically pumped volume is assumed to be the entire surface area of the crystal (2.1×4.8 mm) multiplied by the penetration depth of 810 nm light, which is taken to be approximately $1.15 \mu\text{m}$ [53]. Furthermore, the effect of spin-polarized exciton diffusion can also be taken into account. For an undoped CdTe sample, the exciton diffusion length is expected to be on the order of $1 \mu\text{m}$ [55] at low temperatures. The excitonic diffusion is assumed to be isotropic, so the average depth of penetration caused by exciton diffusion of the initial photo-excited population is taken to be $0.5 \mu\text{m}$. The total affected thickness is thus $1.65 \mu\text{m}$.

Comparing this volume to that of the entire crystal, the number of nuclei contributing to the optically pumped signal is approximately 637 times smaller than that of the thermal equilibrium signal. Correcting for this difference in volume, we have $S(78) / S(290) = (6.7)(637) = 4268$. This value can then be substituted into Equation [31], from which we can then determine the spin temperature to be $T_n = 0.06$ K. This represents a total spin polarization of $p = (N_{\uparrow} - N_{\downarrow}) / (N_{\uparrow} + N_{\downarrow}) = 0.04$.

A similar set of measurements was performed on ^{125}Te at $T = 10$ K.

Figure 17 : ^{125}Te signal dependence on time delay τ_{light} at $T = 10\text{ K}$ for σ - polarization. Integrated signal shown refers to the total NMR peak signal area for a given acquisition, not the maximum value of the peak.

At a sample temperature of 10 K, with continuous irradiation of 500 mW of 1.55 eV light, we found a ^{125}Te relaxation time of $\sim 1900\text{ s}$. The data point at $\tau = 2500\text{ s}$ was selected for comparison. We follow the same procedure as was used for the previous case, starting with the initial measurement of $S_{\text{measured}}(10) / S_{\text{measured}}(290) = 25/2.75 = 9.09$. (In addition to the correction factors used above, the signal acquired at $T = 10\text{ K}$ required only 1 acquisition, while the signal at $T = 290\text{ K}$ was required 4 acquisitions, so we require the average signals be used for a proper comparison. The raw collected data is not averaged, but merely the sum). We have also attempted to estimate the increase in exciton diffusion length at the lower temperature, which increases the total affected thickness to an estimated $3.61\text{ }\mu\text{m}$. Based on our previous estimate (see Figure 12), we assume that nuclear spin diffusion is not significant in this case.

The spin temperature in this case is $T_n = 0.02\text{ K}$, corresponding to a nuclear spin polarization of $p = 0.11$.

5. Conclusions and Recommendations

We have reported the detection of optically enhanced NMR signals from ^{111}Cd , ^{113}Cd , ^{123}Te and ^{125}Te in CdTe. The optical enhancement dependence on photon polarization behaves sinusoidally as expected. Unlike most experiments using different semiconductors, the NMR signal never inverts for any polarization. However, this behaviour, though rare in published results to date, is not without precedence.

Measurements of the magnitude of the signal enhancement show a peak response with a photon polarization corresponding to σ - and a photon energy corresponding to the bandgap of the cubic form of CdTe (at 77 K, this is approximately 1.53 eV). The observed enhancement in the main peak is detectable even at relatively high temperatures, above 77 K. At liquid nitrogen temperatures, the optically enhanced NMR signal is on the order of about 20 times larger than the thermal equilibrium signal. Two minor peaks in the response are clearly explainable, but show some degree of correspondence to the bandgap energies of the hexagonal form. This may be explained by the presence of polytypism in the surface layer of the CdTe crystal used. Polytypism in CdTe is not uncommon and is very dependent on the growth conditions. We caution that there may be other explanations for this peak. However, the sample was etched and the experiment repeated. The minor peaks are clearly reduced and so may have been caused by some phenomena related to surface features.

Previous studies using GaAs and InP has produced a model which predicts the dependence of NMR signal amplitude on optical power. The equation produces a curve which behaves approximately exponentially as it asymptotically approaches the saturation power limit. The saturation optical power in these samples was on the order of 100 mW/cm^2 . Fitting the experimental data to the same model gives a saturation power of 230 mW/cm^2 for this CdTe sample.

A longer irradiation time would be expected to produce a greater NMR signal enhancement. Our experimental data shows that this holds true. For exposure times up to 120 s, it appears that the NMR signal increase is linearly dependent on the exposure time, with the rate increase being different for the different nuclei (i.e. Cd and Te).

Comparison of the relative strengths of the NMR signals of the Cd and Te nuclei do not appear to be consistent with a mechanism for polarizing the bulk nuclear spins that depends on spin diffusion, rather the amplitudes of the NMR signals observed from the four observable spin species are much better predicted by a model incorporating direct polarization of the nuclear spins in the bulk by optically excited electrons or excitons.

5.1 Future Direction

The next steps will be to demonstrate nuclear spin transfer from a semiconductor (optically pumped) into some sort of organic material. One possible experiment might be to use the same CdTe sample with a sufficiently thick, transparent (in the range of energies near the CdTe bandgap) layer of some inert grease (which should contain carbon) on top of the CdTe surface, in physical contact. Due to the fact that the sample will need to be cooled and in a vacuum, a clear barrier may be required to prevent the grease from evaporating.

An NMR cross-polarization sequence will need to be developed and used to attempt to transfer polarization from ^{125}Te (or possibly one of the other nuclei) to the ^{13}C which should be naturally present in the grease. The NMR signal for ^{13}C can then be compared with and without optical excitation of the ^{125}Te to determine the presence of any transfer of enhanced polarization.

Further experiments with different materials are also possible. InP wafers are already available for use, and there has been investigation of optical enhancement of NMR signals in InP in other studies, as well as in this laboratory. These can be coated with some suitable conducting polymer such as AlQ or PPV (or some derivative of) which can be spin cast on using facilities in AMPEL.

Another possibility is to make use of a new organic semiconductor, which has been predicted and derived from first principles. It is based on a layer of ZnSe semiconductor (like CdTe, also II-VI material) bonded between 2 layers of ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$) polymer [56].

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Appendices

Appendix A. NMR Circuit Diagrams

The NMR coil is created by hand wrapping copper wire around a cylindrical rod. The coil labelled **L1** has 5 turns, and was created as a circular coil. One side has been slightly flattened to better fit the sapphire base. The coil diameter (in the direction with flattened edge) is approximately 3.05 mm (0.120") and for the other direction, the coil diameter is approximately 3.30 mm (0.130"). Two nearly identical coils were manufactured, one uses uncoated copper wire, and the other uses coated copper wire. There is no obvious performance difference between the two coils. When designing NMR circuitry, one needs to keep in mind that the circuit values required for optimum operation at low temperature is different from that at room temperature. (Hence the requirement for variable capacitors).

The tuneable capacitors **CV1** (1-22 pF) and **CV2** (0.6-9.5 pF) are non-magnetic air gap capacitors. They are available from Voltronics Corporation, and the relevant Part Numbers are NMQM10GK (0.6-9.5 pF) and NMQM22GK (1-22 pF). Great care must be taken when soldering these capacitors due to the difference in thermal expansion between the metal and the quartz. Silver epoxy is recommended, or if unavailable, use a temperature controlled solder iron with low heat and short work time.

Fixed value capacitors are non-magnetic. These are available from American Technical Ceramics, One Norden Lane, Huntington Station, NY, USA, 11746.

The circuit used for ^{125}Te is shown below in Figure 18. The fixed capacitor is labelled "150K" and has a value of 15 pF.

Figure 18 : NMR Circuit for ^{125}Te

The circuit used for ^{123}Te is shown in Figure 19. The fixed capacitor is labelled "3R9" and has a value of 3.9 pF.

Figure 19 : NMR circuit for ^{123}Te

The circuit used for both ^{113}Cd and ^{111}Cd is shown below, it is capable of tuning to the resonance frequency of both isotopes. The two fixed capacitors are labelled "2R2C" and "100F", with values 22 pF and 1.0 pF, respectively.

Figure 20 : NMR circuit for Cd

For both circuits, the shape of the resonance peak was observed on a sweep generator when not in the NMR magnet. The width and magnitude of the resonant peak was comparable in both cases when tuned to the appropriate frequencies. This is some indication that the Q of the circuits are not vastly different, which is important to note when comparing signal amplitudes from the various nuclei.

Appendix B. Signal Conditioning

The transmitted signal is filtered (low power) before it is fed to the transmit amplifier to remove unwanted frequency components. A 100 MHz low-pass filter is employed in all cases, except when dealing with ^{125}Te , where a 100 MHz high-pass filter is used in conjunction with a 150 MHz low-pass filter to create a band-pass filter.

A second filter (high power) was used immediately prior to transmission through the coil. A 100 MHz low-pass filter is employed for all cases, except when dealing with ^{125}Te , where a 200 MHz low-pass filter was used.

The receiver utilized the same low power filter types as the transmitter, installed immediate before the amplifier. i.e. 100 MHz low-pass or 100 MHz high-pass combined with 150 MHz low-pass.

The receive amplifier has 3 attenuation settings available which can be used individually or together, and are activated using the toggle switches on the front panel. Settings available are -5 dB, -10 dB and -20 dB. These attenuation settings can become necessary because the amplifier operates at a fixed gain. If the resulting output signal is too large, it can saturate the A/D converter.

Experimental data acquired for this experiment used no (i.e. 0dB) attenuation.

Note: To determine if any attenuation is necessary, take a single acquisition of data without any attenuation, if the raw FID has a maximum amplitude close or equal to 32768, then attenuation is necessary. Activate the minimum required amount of attenuation so that no expected signal will exceed this value. This limitation applies for a single acquisition only. The sum of multiple acquisitions can exceed 32768, as the software is capable of handling larger integers.

Sample cooling is normally provided by gas flow from a pressurized dewar of liquid helium or nitrogen. This is the preferred method if available. Specific details and procedures for performing the cooling are described in Appendix E.

Temperature control of the cryostat is provided by a Lakeshore Model 340 Temperature Controller which connects to the cryostat which can monitor and heat (up to 25W capacity) the cold-finger as required to maintain the temperature.

Unfortunately, a great deal of spurious noise can be coupled through the connector. If the liquid nitrogen filling method is used, then once the required temperature is reached, it is recommended to disconnect the temperature controller. This method cannot be used for the liquid helium flow method for any temperature above 4.3 K because of the requirement for temperature monitoring and control.

Appendix C. CdTe Crystal Analysis

Unfortunately, no data other than the resistivity ($10^9 \Omega\cdot\text{cm}$) was provided with the CdTe sample. Upon visual inspection, it appears that both large faces of the crystal have been polished.

Appendix C.1. X-ray diffraction

X-ray diffraction scattering measurements were performed on one face of the crystal using a powder diffraction setup. (The crystal had not been etched with HCl). With one edge of the crystal oriented perpendicular to the incident beam, this provides a measure of the primary orientation of the crystal, and other major planes which satisfy the Bragg criteria. If the crystal is not oriented properly in the crystal holder, it is unlikely to be able to observe any measurements using the powder diffraction setup because the scattered x-ray may not strike the detector.

Figure 21 : X-ray Bragg diffraction

The x-ray diffraction spectrometer will rotate the sample with respect to the x-ray source and usually provides a measurement of 2θ . A peak is observed in the spectrum when the angle θ satisfies the requirement:

$$n\lambda = 2d \sin \theta \quad [32]$$

where:

- λ = wavelength of incident x-rays
 d = lattice spacing
 θ = angle of incidence of the x-ray with respect to the plane of the lattice

If the lattice spacing between the atomic planes is known, and the incident energy of the beam is also known, then it is possible to calculate the position of the expected peaks using the above formula.

Appendix C.2.CdTe lattice properties

Figure 22 : CdTe unit cell

Crystal properties can be found in Pearson's Handbook Vol. II. There are 24 atoms in the unit cell. With reference to Te, the coordinates for each atom are given in the table below.

Table 3 : Atom coordinates for CdTe unit cell

Atom	x [Å]	y [Å]	z [Å]
Te	0.000000	0.000000	0.000000
Cd	0.000000	2.629000	0.756625
Te	0.000000	0.000000	3.026500
Cd	0.000000	2.629000	3.783125
Te	0.000000	0.000000	6.053000
Te	0.000000	5.258000	0.000000
Te	0.000000	5.258000	3.026500
Te	0.000000	5.258000	6.053000
Te	2.810200	0.000000	0.000000
Cd	2.810200	2.629000	0.756625
Te	2.810200	0.000000	3.026500
Cd	2.810200	2.629000	3.783125
Te	2.810200	0.000000	6.053000
Te	2.810200	5.258000	0.000000
Te	2.810200	5.258000	3.026500
Te	2.810200	5.258000	6.053000
Te	5.620400	0.000000	0.000000
Cd	5.620400	2.629000	0.756625
Te	5.620400	0.000000	3.026500
Cd	5.620400	2.629000	3.783125
Te	5.620400	0.000000	6.053000
Te	5.620400	5.258000	0.000000
Te	5.620400	5.258000	3.026500
Te	5.620400	5.258000	6.053000

Appendix C.3.Experimental Setup and Results

The crystal holder was relatively large compared to the target crystal, so scatter from the holder was expected. Therefore, an initial background measurement using just the holder was performed prior to the diffraction measurements on the CdTe crystal. Results from both measurements were subtracted to obtain the contribution from the crystal.

Figure 23 : Full x-ray diffraction spectrum

Figure 23 shows the full spectrum take from the measurement. Figure 24 shows a smaller range of the section which is comparable to the data available from prior literature [57][58].

Figure 24 : Magnification of relevant region

The corresponding peaks are listed in Table 4, with data taken from [57].

Table 4 : X-ray diffraction peaks for CdTe

Experimental	Literature	zincblende (hkl)	wurtzite (hkl)
24.65°	24°	(002)	(111)
-	32-34°	-	(102)
38.25°	37-38°	(220)	(110)
-	42-43°	-	(103)
44.50°	45-46°	(311)	(112)
-	54°	-	(202)
64.85°	65-65.5°	(331)	(211)
-	71°	(422)	(300)
78.00°	78-79°	(511)	(205)
82.15°	no data	no data	no data

Based on the measured data, it is likely that the crystal orientation (as used in our experiment) is (111). This is also the usual orientation for CdTe crystal growth.

Appendix D. Laser usage and maintenance

The laser is a tuneable Ti:Sapphire laser capable of up to 1 W output. It is pumped by a 532 nm diode laser which is normally rated to 5 W, but is capable of 5.50 W for short periods.

The Ti:Sapphire laser uses 3 interchangeable bi-refringent filters to cover a wide range of possible output wavelengths. Note that the full optical output of 1 W is not practically achievable across all wavelengths. Tuning is achieved by using a micrometer knob at the side of the laser. The approximate calibrations are shown below.

Figure 25 : Laser calibration settings

The 3 filters are labelled SW (short wavelength), MW (medium wavelength) and LW (long wavelength). The SW and LW filters have 2 discontinuous regions of operation. For best optical power output, the laser needs to be tuned each time the wavelength is changed.

Appendix D.1.Laser Maintenance

If the laser has not been used in a long time, or the bi-refracting tuner elements have been changed, it is necessary to re-tune the laser for optimum performance. It is greatly easier to tune the laser if it is in fact still lasing, so it is not advised to wait a long period of time (e.g. months) between tuning.

Before you start tuning, set up the optical power meter and adjust the laser to some convenient output level, e.g. 100 mW. It is easiest if you set the power meter in the special "Tuning" mode rather than the standard mode use for monitoring the output power.

For most purposes, the tuning knobs accessible outside the laser will be sufficient to tune the laser. Start with the vertical tuning knobs and work in a specific order (i.e. Mirror 1, Mirror 3, etc.). The specific order usually doesn't matter as long as you follow it.

After you have tuned all the vertical settings, follow exactly the same order while tuning the horizontal adjustments. Repeat the procedure again for vertical, then horizontal adjustments, again maintaining the same order. Mirrors M6 and P3 usually have the greatest affect.

If this is still insufficient to achieve the desired power, you may have to adjust the internal mirrors (especially if a tuner element has been changed). In this case, follow the same procedure as before, but include the internal mirrors as well. In addition to M6 and P3, the internal M2 and M4 elements usually have the greatest affect. 3 or 4 repetitions of the tuning sequence are usually sufficient to align the mirrors to their optimum setting.

If the desired power still cannot be achieved, it is likely that several of the surfaces are dirty and cleaning is required. Always use a clean set of latex or vinyl gloves (powder free) to avoid contaminating the optical surfaces with oils. Methanol or acetone can be used for cleaning, wiping with lens paper. Some general tips:

- Apply the methanol to the lens paper first, shake off the excess before wiping the optics
- Clean with a single swipe in 1 direction only. Do not rub the surface back and forth!
- Do not re-use the lens paper! Lens paper is relatively inexpensive compared to the cost of optics.

In general, any of the optical surfaces with a horizontal component will have the greatest change after cleaning. This includes the top side of the Ti:Sapphire crystal itself. Components which are mounted vertically tend to benefit little from frequent cleaning.

Lastly, if the desired optical power still cannot be achieved, keep in mind that the maximum rated power (1 mW) is only possible for certain wavelengths.

Appendix D.2.Wavelength meter

The Wavemate wavelength meter requires a 15 minute warm-up time before it can be used. Further, on initial use after power-on, the OFFSET should be set to "ZEROAUTO", otherwise the readings will not be consistent or accurate. After the automatic offset calibration, the OFFSET can be returned to "ZEROMANUAL" mode if no significant changes are made to the laser.

At most settings used for the experiment, the optical power, even after the beam splitter, is generally too high for the wavelength meter. 2 optical attenuators in the beam path is generally sufficient to decrease the optical power to a range useable by the wavelength meter. At higher powers, it may be necessary to insert a 3rd attenuator (if available), or usually 2 layers of lens paper also work in practice.

Appendix D.3.Optical Power Meter

No special setup or preparation is required for usage of the optical power meter, except that one needs to ensure that the wavelength is set at the range you will be operating in, or else readings will fluctuate.

Appendix E. Cooling the cryostat

Use liquid He for temperatures between 4.3 K and 77 K. For temperatures above 77 K, it is more economical to use liquid N₂.

Appendix E.1. Preparation of the cryostat

When operating at low temperatures, it is necessary to first pump out the interior of the cryostat, in the sample chamber, to create a good vacuum. For liquid nitrogen temperatures, allow approximately 1 day of pumping with a good mechanical pump to create a vacuum of $\sim 10^{-6}$ torr. Depending on the sample and other materials used, some outgassing may occur and a longer period of time may be required.

If lower temperatures are required, (i.e. with liquid helium), in addition to mechanical pumping, one generally requires an additional 12 hours of pumping with a good diffusion pump to further increase the vacuum to the order of 10^{-8} torr or better.

At the same time, it is very important to ensure that the chamber for the liquid helium / nitrogen flow in the cryostat is free of moisture. If there is too much water in the chamber, the resulting ice can expand and cause physical damage to the cryostat. Furthermore, it will significantly increase the time it takes to cool the experiment down to operating temperatures. When it is completely dry, it should take approximately 15 minutes to cool the cold-finger down to 77 K (using the liquid nitrogen filling method), and less than 2 L of liquid nitrogen. If water is present, the time will increase to several hours.

The fastest method of drying out the chamber is by blowing dry air through the cryostat. It should take no longer than 10 to 15 minutes even for a very wet chamber (i.e. up to about 100 mL of water). If no dry air is present, a mechanical vacuum pump will suffice, and for any reasonable level of moisture (e.g. a few mL of condensation), 10 to 15 minutes will suffice. For large quantities of moisture, the vacuum pump will require significantly more time.

Appendix E.2. Liquid helium flow

This is a standard method, and utilizes a Janis Research ST-VP cooling line to control the helium flow. Unlike the liquid helium transfer lines, this line has a valve to control the flow rate. Ensure that the valve is closed (i.e. no flow) prior to starting the procedure.

Fit one end of the line into the cryostat, inserting it all, or close to all, the way to the bottom and tighten the seal. The outlet end of the cryostat should be fitted to a mechanical vacuum pump, which should be turned on at this point.

Next, fit the other end of the line into the liquid helium dewar, and **slowly** feed it in. The tip of the line has touched the liquid when you observe the pressure gauge start to increase. At this point, insert the line 2-3 cm deeper. Tighten the seals, and tie up the line to make sure it will not slip down into the dewar.

At this point, open the valve on the line approximately 2 full turns. The temperature should start to slowly increase, this is normal behaviour and may continue for some time, anywhere from 15-30 minutes. After this time, you will observe the temperature decrease rapidly. At approximately 270 K (the exact temperature is not important), turn off the vacuum pump and replace it with a rubber stopper and hose to funnel away excess cold gas. Do not turn off the vacuum pump too soon, else the temperature will start to rise again.

If the diffusion pump is in use with liquid nitrogen, be sure to close off the valve to the pump before the cryostat temperature drops below 77 K. If liquid nitrogen is not used, the valve should be closed before the cooling starts.

Monitor the pressure gauge on the dewar and ensure that it does not exceed 5 psi. It is best to keep the pressure between 1 and 2 psi. It will take some time (maybe up to an hour or more) to reach 10 K. This method. Be patient! **Do not** try to rush the process by increasing the pressure and flow, as it will slow down the entire procedure and waste significantly more liquid helium. During the course of a typical experiment lasting 4-8 hours, you should use no more than 4 L of helium. Rushing the procedure can cause over 20 L to be used, and present possible safety hazards due to highly pressurized liquid helium.

Appendix E.3.Liquid Nitrogen Fill Method

For liquid nitrogen temperatures and above, it is generally more economical to utilize liquid nitrogen instead of liquid helium. However, a suitable transfer line and dewar are not available, so a method using liquid nitrogen filling is used. The drawback is that this allows cooling only a single temperature, 77 K.

An insulated funnel with large capacity is fitted on top of the cryostat, where a transfer line normally fits. At the outlet end, a rubber hose with a stopcock is fitted on to drain any excess liquid nitrogen away from the magnet and cryostat. Liquid nitrogen is then poured into the funnel, cooling the cryostat. Covering the top of the funnel will minimize any ice buildup. It is generally preferable to keep the funnel as full as possible so that no water (ice) enters the cryostat.

Appendix E.4.Accurate Determination of Sample Temperature

Regardless of the method used for cooling, it is important to note that the temperature reading from the cold-finger is generally not reflecting accurately the temperature of the sample or the chamber unless sufficient time is allowed for all components to reach thermal equilibrium. A second Cernox RTD placed in thermal contact with the sample will provide a more accurate reading.

If a second RTD is not available, or not practical, one can monitor the state of the system by observing the tune of the NMR probe circuit. The variable capacitors will have to be adjusted continuously as the probe cools to match the desired resonance frequency. When the tune remains constant for a sufficiently long time (e.g. 10-15 minutes), then all the components of the system have reached a thermal equilibrium, which is presumably the reading provided by the Cernox RTD embedded within the cold finger.

Appendix F. Cernox RTD Specifications

The following data is reproduced from LakeShore literature. The relevant RTD is the Hermetic Ceramic Package (SD).

Table 5 : Properties of Cernox RTD

	Unpackaged Chip (BC) (BG) (BR)	Hermetic Ceramic Package (SD)	Copper Canister Package (AA)
Temperature			
Useful Range			
Minimum	0.30 K (model dependent)	0.30 K (model dependent)	0.30 K (model dependent)
Maximum	325 K (420 K, Cernox HT)	325 K (420 K, Cernox HT)	325 K (420 K, Cernox)
Maximum Storage Temperature	325 K	325 K	325 K
Standard Curve	Not applicable	Not applicable	Not applicable
Sensitivity (dR/dT) (typical)	See plots	See plots	See plots
Dimensionless Sensitivity	See plots	See plots	See plots
Accuracy (Interchangeability)	Not applicable	Not applicable	Not applicable
Accuracy (SoftCal™)	Not applicable	Not applicable	Not applicable
Accuracy (Calibrated)²	± 5 mK at T < 10K; ± 20 mK at 20 K; ± 35 mK at 50 K; ± 140 mK at 300 K; (model dependent)		
Stability¹ Short-term	±0.003 K at 4.2 K	±0.003 K at 4.2K	±0.003 K at 4.2K
Stability¹ Long-term (per year)	± 25 mK (1 to 100K); 0.05% of temperature (100 to 325 K) (all models)		
Thermal Response Time	1.5 ms at 4.2 K 50 ms at 77 K 135 ms at 273 K	15 ms at 4.2 K 0.25 seconds at 77 K 0.8 seconds at 273 K	0.4 seconds at 4.2 K 2 seconds at 77 K 1.0 seconds at 273 K
Recommended Recalibration Schedule	Annual	Annual	Annual
Excitation			
Recommended	10 mV (1.4 to 325 K) (all models) Measurement below 1 K should be performed with an AC resistance bridge. Typical operating power is 10-11 W at 0.5 K (CX-1030 only) ³		
Maximum Power Before Damage	10 ⁻⁴ W, 10 mA or 1 V whichever is less (all models)		
Dissipation at Rated Excitation	Typical 10 ⁻⁵ W at 300K; 10 ⁻⁷ W at 4.2 K; 10 ⁻¹³ W at 0.3 K (model and temperature dependent)		
Units Range (volts or ohms)	Typical 20 W at room temperature to 100,000 W at lower temperature limit (model dependent)		
Lead Wire Configuration	See lead specification below	Two lead, no polarity	Four lead, color coded
Materials in the Sensor/Construction	Ceramic oxynitride, gold pads, and sapphire substrate (chip for all models)	Chip mounted on sapphire base with alumina body and lid. Mo/Mn with nickel and gold plating on base and lid.	Chip mounted in a gold plated cylindrical copper can.

Optical Enhancement of NMR Signals in CdTe

		Gold-tin solder as hermetic lid seal.	
Size in Millimeters	0.75 x 1.0 x 0.25 to 0.38 mm	3.2 mm x 1.9 mm base x 1mm	3 mm diameter x 8.5 mm long
Mass	< 3.0 milligrams	Approximately 40 milligrams	Approximately 400 milligrams
Leads			
Size	---	0.2 mm diameter x 25 mm long	0.24 mm diameter x 15 cm long
Number	BR: none; BG: two; BC: two	Two (2)	Four (4)
Material	BG: gold;BC: copper	Phosphor-bronze	Phosphor-bronze
Internal Atmosphere	Not applicable	Vacuum	Helium 4 (4He) is standard
Radiation Effects	Recommended for use in radiation environments (see reference section)		
Magnetic Fields	Recommended for use in magnetic fields at low temperatures. The magnetoresistance is typically negligibly small above about 30 K and not significantly affected by orientation relative to the magnetic field. Refer to plots of temperature errors (all models)		
ESD Sensitivity	Not applicable	Not applicable	Not applicable
Noise Sensitivity	Not applicable	Not applicable	Not applicable

Notes:

(1) Long-term stability data is obtained by subjecting sensor to 200 thermal shocks from 305 K to 77 K. Calibration shifts are measured over the temperature range from 1.4 K to 330 K. Short-term stability data is obtained by subjecting sensor to ten thermal shocks from 305 K to 4.2 K. Data is taken at 4.2 K only.

(2) Bare chip sensors can only be calibrated after attaching gold wire leads. The user must remove the ball bonded leads if they are not desired. The bond pads are large enough for additional bonds.

Typical Calibration Shifts

(3) Typical temperature reading errors for operation of Model CX-1050 sensors in magnetic fields at temperatures from 20.3 K to 286 K

"Low temperature thermometry in high magnetic fields VII. Cernox™ sensors to 32 T," B.L. Brandt, D.W. Liu and L.G. Rubin; Rev. Sci. Instrum., Vol. 70, No. 1, 1999, pp 104-110

Appendix G. Sample Preparation and Maintenance

The CdTe sample is already polished from the manufacturer. To clean the surface of the crystal, methanol or acetone was used to remove any grease or oils.

To clean off the Apiezon grease, the recommended procedure is to use Xylene with an Isopropyl alcohol rinse. If that is not available, it is possible to get a relatively clean surface with liberal application of acetone and light rubbing on low abrasion, lint-free paper.

Appendix G.1. Notes about Apiezon® N:

This general purpose grease enhances thermal contact to sensors and provides a temporary method for mounting temperature sensors. The grease is pliable at room temperatures and solidifies at cryogenic temperatures. This makes it easy to apply and remove the sensor (without damage) at room temperature. The grease is not an adhesive and will not necessarily hold a sensor or wires in place without some mechanical aid, such as a spring clip or tape. It is very good for sensors inserted into holes. Contains a high molecular weight polymeric hydrocarbon additive which gives it a tenacious, rubbery consistency allowing the grease to form a cushion between mating surfaces.

Table 6 : Properties of Apiezon® Grease

Apiezon® Grease	Type N	Type H
Approximate melting point	316 K (43 °C)	523 K (250 °C)
Thermal Conductivity		
(W·m ⁻¹ ·K ⁻¹)		
293 K (20 °C)	0.19	0.22
4 K (-269 °C)	0.005	
1 K (-272 °C)	0.001 W/m-K	
4.2 K (-269 °C)	0.005 W/m-K	
100 K (-173 °C)	0.15 W/m-K	
300 K (27 °C)	0.44 W/m-K	
Volume resistivity (ohm m)	2 x 10 ¹⁶	4.6 x 10 ¹³
Thermal expansion coefficient	0	0
Vapor pressure (torr) 293 K (20 °C)	2 x 10 ⁻⁹	2.7 x 10 ⁻⁹
Solvent system	Hydrocarbons or chlorinated solvents	

Appendix H. Spin diffusion

Appendix H.1. NMR Signal dependence on the diffusion constant

For diffusion from a point source, we should have:

$$U_t = D \nabla^2 U \quad [33]$$

where:

D	=	nuclear spin diffusion constant
U	=	distribution of nuclear spin polarization, in general a function of space and time
U_t	=	1st derivative, with respect to time t , of U .

with $0 < x < \infty$, $t \geq 0$. And, we have the boundary conditions that $U(r,0) = 0$ and $U(0,t) = U_0$. That is, there is nothing anywhere initially, except at the very centre, where a constant value is maintained for all time. (We assume here that during the time scales we are interested in, we are constantly supplying a source of spins, i.e. always optically pumping during this time).

In spherical coordinates, the Laplacian is:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin^2 \phi} \frac{\partial^2}{\partial \theta^2} + \frac{\cos \phi}{r^2 \sin \phi} \frac{\partial}{\partial \phi} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \quad [34]$$

If we assume that diffusion is equally likely in all directions, and we therefore have only a dependence on r , then the differential equation simplifies greatly:

$$U_t = D \left(\frac{\partial^2}{\partial r^2} (U) + \frac{2}{r} \frac{\partial}{\partial r} (U) \right) \quad [35]$$

This can then be solved using the method of Laplace Transform. The transformed equation is then:

$$sV(r,s) = D \left(\frac{\partial^2}{\partial r^2} V(r,s) + \frac{2}{r} \frac{\partial}{\partial r} V(r,s) \right) \quad [36]$$

Where $V(r,s)$ is the Laplace Transform of $U(r,t)$. We can verify that a solution of this equation is:

$$V(r, s) = \frac{e^{-\sqrt{\frac{s}{D}} r}}{r} \quad [37]$$

Now applying the inverse Laplace Transform:

$$U(r, t) = \int_{-\infty}^{+\infty} e^{st} \frac{e^{-\sqrt{\frac{s}{D}} r}}{r} ds \quad [38]$$

To get the NMR signal, we need to integrate over all-space.

$$n(t) = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 \left(\int_{-\infty}^{+\infty} e^{st} \frac{e^{-\sqrt{\frac{s}{D}} r}}{r} ds \right) dr \quad [39]$$

Switching the order of the integration:

$$n(t) = 4\pi \int_{-\infty}^{+\infty} \left(\int_0^\infty r e^{st} e^{-\sqrt{\frac{s}{D}} r} dr \right) ds \quad [40]$$

$$n(t) = 4\pi \int_{-\infty}^{+\infty} e^{st} \frac{D}{s} ds = 4\pi D \int_{-\infty}^{+\infty} e^{st} \frac{1}{s} ds \quad [41]$$

At this point, we no longer need to complete the integration, as we know that the signal is simply proportional to D . Numerical simulations also show a linear dependence on D as predicted by calculations.

Appendix H.2. Dependence of diffusion constant on abundance

Since we have determined that the NMR signal amplitude should depend linearly on the diffusion constant D , it is then important to figure out how this diffusion constant varies with abundance of NMR observable nuclei. Given that CdTe has 4 different observable nuclei in varying abundances, the correlation of observed signal with abundance should give some clue as to the processes responsible for optical enhancement of the NMR signal.

When the nuclear abundance of an NMR observable species is high (i.e. 100% or sufficiently close), then the diffusion constant can be adequately predicted using a mean-field approximation. However, in the case of CdTe, the most abundance species (Cd) are less than 13% abundant, so it is not obvious that this approximation should hold.

A numerical simulation of the diffusion constant dependence on nuclear abundance showed that below a critical level, the diffusion constant drops significantly below the mean-field average.

Figure 26 : Numerical simulation of diffusion constant dependence on nuclear abundance.

As can be seen in Figure 17, the simulation is not well modelled by a mean-field approximation ($\propto A^{1/3}$) at low nuclear abundances. A better model, suggested by percolation theory ($\propto A^{1/3}$ with cutoff), provides a good fit up until the cutoff limit.

The simulation results are similar to that shown in previous work [49][50]. The behaviour of the simulation at very low abundances would suggest some sort of asymptotic behaviour. However, we believe this is an artifact of the simulation, where a spin is simply diffusing back and forth between a handful of eligible sites. This artifact should disappear with the use of a sufficiently large lattice. Unfortunately, we are currently constrained by the computing resources from running larger simulations.

Simulation code is written in Matlab (see code listing in following sections). The script `sim_spindiff.m` is merely a "shell" that calls up the actual simulation and keeps track of some values for the purposes of averaging. The bulk of the computation is accomplished by the function `spindiff.m`, which will simulate spin diffusion on a 3-D lattice. The limitation is that it only considers the nearest neighbours, and does not account for the probability of spin diffusion to a farther site. Contributions from all nuclei other than the nearest ones are neglected.

Appendix H.3. sim_spindiff.m

```
NumAvg=100;

D=zeros(NumAvg,100);
D2=zeros(NumAvg,100);
steps = 29;

tic
for (abund_count = 1:100)
    abund_count
    toc
    for (navg = 1:NumAvg)
        [t,d,x,y,z,lattice] = spindiff(abund_count);
        % b = regress(d',[t',ones(length(t),1)]);
        % D(navg,abund_count) = b(1);
        final_distance = sqrt((x(steps)-x(1))^2 + (y(steps)-y(1))^2 + (z(steps)-z(1))^2);
        D(navg,abund_count) = final_distance / t(length(t));
        D2(navg,abund_count) = final_distance^2 / t(length(t));
    end
end
Diff_sum = sum(D);
Diff_sum2 = sum(D2);
Diff_avg = Diff_sum/NumAvg;
```

Appendix H.4. spindiff.m

```
function [ time, distance, x_hist, y_hist, z_hist, lattice ] = spindiff( abundance )
%spindiff calculates the diffusion constant at a given abundance
% Usage:
%   spindiff(A)
% where:
%   A = abundance in percent. e.g. spindiff(90) for 90%
lattice_size = 80;
iterations = 40;

% Generate the lattice
if (abundance == 0),
    lattice = zeros(lattice_size,lattice_size,lattice_size);
end
if (abundance == 100)
    lattice = ones(lattice_size,lattice_size,lattice_size);
else
    % Assuming rand() function is good, this should
    % generate approximately the right distribution.
    actual_abundance = 999;
    while(actual_abundance ~= abundance/100),
        lattice = floor(rand(lattice_size,lattice_size,lattice_size)+abundance/100);
        actual_abundance = sum(sum(abs(lattice))) / lattice_size^2;
    end
end

% Start at center of the lattice
x = round(lattice_size/2);
y = round(lattice_size/2);
z = round(lattice_size/2);
time(1) = 0;
distance(1) = 0;

% Flag this point with something, say -1.
lattice(x,y,z) = -1;

% Initialize the neighbour count
nbr_count = 0;

% This loop is to run the number of iterations you want
run_count = 1;
while (run_count < iterations),

    % This loop is to search the nearest neighbours until
    % you find a suitable neighbour.
    % It starts with the inner-most "radius" and keeps expanding
    % out until one is found.
    n = 1;

    % r_near is a "flag" to keep track of the current nearest
    % set to some suitably large number to start.
    r_near = 99999;

    while (n <= lattice_size),
        for xn = -n:n,
            xt = x + xn;
            for yn = -n:n,
                yt = y + yn;
                for zn = -n:n,
                    zt = z + zn;
                    % Check for out of bounds
                    if ((xt > 0) & (yt > 0) & (zt > 0) & ~(xt == x) & (yt == y) & (zt == z)) &
(xt <= lattice_size) & (yt <= lattice_size) & (zt <= lattice_size)),
                        % If the neighbour exists, add it to the list.
                        % Note "flaw" here, the diagonals are actually farther, not
                        % at the same radius. Either fix by checking if it matches
                        % closest one in list, or weight transition probability
                        % by distance
                        r_xy = sqrt(abs(xt - x)^2 + abs(yt - y)^2);
                        r_xyz = sqrt(r_xy^2 + abs(zt - z)^2);
```

```

% Factor in dipolar coupling
dipole_angle = abs(3 * (r_xy^2 / r_xyz^2) - 1);
dip_prob = round(10 * dipole_angle);
r_prob = round(10 * r_xyz);
if (lattice(xt,yt,z) == 1),
    % This is to allow all directions, but factor
    % in probability due to angular dependence and extra distance
    r_near(nbr_count+1:nbr_count+dip_prob+r_prob+1) = r_xyz;
    nbr_list_x(nbr_count+1:nbr_count+dip_prob+r_prob+1) = xt;
    nbr_list_y(nbr_count+1:nbr_count+dip_prob+r_prob+1) = yt;
    nbr_list_z(nbr_count+1:nbr_count+dip_prob+r_prob+1) = zt;
    nbr_dipole(nbr_count+1:nbr_count+dip_prob+r_prob+1) = dipole_angle;
    nbr_count = nbr_count + dip_prob + r_prob + 1;
end
end
end % This ends the z-loop
end % This ends the y-loop
end % This ends the x-loop

% If we have nearest eligible neighbours, stop searching outer radii
if (nbr_count ~= 0),
    n = lattice_size+1;
end
n = n + 1;
end

% Now go through the list of nearest neighbours and
% randomly pick one.
rdir = round(rand(1)*(nbr_count-1))+1;

% Transfer the spin to the new location
lattice(x,y,z) = 1;
x_hist(run_count) = x;
y_hist(run_count) = y;
z_hist(run_count) = z;
x = nbr_list_x(rdir);
y = nbr_list_y(rdir);
z = nbr_list_z(rdir);
lattice(x,y,z) = -1;

% Calculate the distance to that neighbour and time required
distance(run_count+1) = distance(run_count) + r_near(rdir);
time(run_count+1) = time(run_count) + ((r_near(rdir))^3)/nbr_dipole(rdir);

% Need to clear the list of neighbours before next iteration.
r_near = 0;
nbr_list_x = 0;
nbr_list_y = 0;
nbr_list_z = 0;
nbr_dipole = 0;
nbr_count = 0;

run_count = run_count + 1;

end

%x_hist
%y_hist
%z_hist
%lattice

% x_hist and y_hist contain a list of all the steps. Uncomment for verbose running.

```

Appendix I. Program Listings

Appendix I.1. Presat_OnePulse.x

```
/******
Name: Presat_OnePulse.x
Version: 1.0
Author: Isaac Leung / Matt Grinder
Date: 2003-05-28
Description: Simple one-pulse with pre-saturation sequence
Channels: 1
Sequence: SAT-90-Acquire
History:
0.1 - Initial implementation by Matt Grinder
1.0 - Tweaked and added descriptive goodies.
*****/

#include "pulse.h"

int main()
{
    float pw1,pw2;
    float d1;
    float PPO;
    float rd;
    float sfloffset;
    float amplitudel;
    double sf1,sf,sf2;
    int acqn;
    int npul,i;
    float space,tau;

    /* This is the phase sequence for pulses */
    float phase0[8]={0.,0.,90.,90.,180.,180.,270.,270.};
    float phase1[8]={90.,270.,180.,0.,270.,90.,0.,180.};

    /* This is the phase for the receiver */
    int ph_rec[8]={1,3,2,0,3,1,0,2};

    /* Extra text variables for describing the experiment. Optional */
    char Compound[255];
    char Nucleus[255];
    char Notes[255];

    pulse_program_init();
    do {
        /* Get the user values for the various parameters */
        GET_PARAMETER_FLOAT( sfloffset);
        GET_PARAMETER_FLOAT( amplitudel);
        GET_PARAMETER_FLOAT( pw1); //pulse width for first chain of pulses
        GET_PARAMETER_FLOAT( pw2 ); //pulse width for last pulse
        GET_PARAMETER_FLOAT( d1 );
        GET_PARAMETER_FLOAT( PPO );
        GET_PARAMETER_FLOAT( rd );
        GET_PARAMETER_DOUBLE(sf1); // this is in MHz
        GET_PARAMETER_DOUBLE(sf2); // this is in MHz
        GET_PARAMETER_INT(npul); // this is an integer
        GET_PARAMETER_FLOAT(space); // this is in ms (space between pulses in pulse chain)
        GET_PARAMETER_FLOAT(tau); // this is in ms
        GET_PARAMETER_TEXT(Compound);
        GET_PARAMETER_TEXT(Nucleus);
        GET_PARAMETER_TEXT(Notes);

        acqn = get_acqn();

        begin();
    } while (1);
}
```

```
/* Set the Frequency for Channel 1 and 2 */
sf= sf1+((double) sfloffset)/1e6;
set_freq1(sf);
set_freq2(sf2);

/* Amplitude and Phase need to be set on 1st use. */
EVENT d1 {PHASE1,phase0[acqn%8]} {RF1_BLNK,1} {AMPL,amplitudel} ;

/* This is the pre-saturation sequence. npul = number of pre-sat pulses */
for (i=0 ; i<npul ; i++) {
    EVENT pw1 { RF1, 1} {RF1_BLNK,1} {PHASE1,phase0[acqn%8]};
    EVENT space {RF1_BLNK,1};
}
/* END Pre-Sat Sequence */

/* This sets the delay time between the pre-sat pulse and the "signal" pulse */
if (tau-space < 5e-06)
    EVENT tau-space;
else{
    EVENT tau-space-(5e-06) ;
    EVENT 5e-06;
}

/* BEGIN PULSE SEQUENCE */
EVENT pw2 {RF1, 1} {RF1_BLNK,1} {PHASE1,phase1[acqn%8]};
EVENT rd {AMPL,0.0};
/* END PULSE SEQUENCE */

/* Data Acquisition Sequence */
/* Usually don't have to modify */
SYNC_DSP;
EVENT get_dwell()*get_npts() {AD_STAQ,1} {RCVR_GATE,1};

/* This is the delay between multiple acquisitions (for averaging) */
/* Usually don't have to modify this */
EVENT PPO {PP_OVER, 1};

} while( ready( ph_rec[acqn%8] ) == P_PROGRAM_CALC );

done();
return 0;
}
```

Appendix I.2. Presat_OnePulse_Shutter.x

```
/******
Name: Presat_OnePulse_Shutter.x
Version: 1.0
Author: Isaac Leung / Matt Grinder
Date: 2003-05-28
Description: Simple one-pulse with pre-saturation sequence, with optical shutter control
Channels: 1 + Optical Shutter
Sequence: SAT-90-Acquire
History:
0.1 - Initial implementation by Matt Grinder
1.0 - Tweaked and added descriptive goodies.
*****/

#include "pulse.h"

int main()
{
    float pw1,pw2;
    float d1;
    float PPO;
    float rd;
    float sfloffset;
    double sf1,sf,sf2;
    int acqn;
    int Npresat_pul,i;
    float tau_1,tau_d,N90_shutter,delay_sh,space_sh;
    float presat_gap;

    /* This is the phase sequence for pulses */
    float phase0[8]={0.,0.,90.,90.,180.,180.,270.,270.};
    float phase1[8]={90.,270.,180.,0.,270.,90.,0.,180.};

    /* This is the phase for the receiver */
    int ph_rec[8]={1,3,2,0,3,1,0,2};

    /* Extra text variables for describing the experiment. Optional */
    char Compound[255];
    char Nucleus[255];
    char Notes[255];

    pulse_program_init();
    do {
        /* Get the user values for the various parameters */
        GET_PARAMETER_FLOAT( sfloffset);
        GET_PARAMETER_FLOAT( pw1); //pulse width for first chain of pulses
        GET_PARAMETER_FLOAT( pw2 ); //pulse width for last pulse
        GET_PARAMETER_FLOAT( d1 );
        GET_PARAMETER_FLOAT( PPO );
        GET_PARAMETER_FLOAT( rd );
        GET_PARAMETER_DOUBLE(sf1); // this is in MHz
        GET_PARAMETER_DOUBLE(sf2); // this is in MHz
        GET_PARAMETER_INT(Npresat_pul); // this is an integer
        GET_PARAMETER_FLOAT(presat_gap); // this is in ms (space between pulses in pulse chain)
        GET_PARAMETER_FLOAT(tau_1); // this is in ms
        GET_PARAMETER_FLOAT(tau_d); // this is in ms
        GET_PARAMETER_TEXT(Compound);
        GET_PARAMETER_TEXT(Nucleus);
        GET_PARAMETER_TEXT(Notes);

        acqn = get_acqn();

        /* This is the gap between pulses in the presat sequence in [ms] */
        //presat_gap = 0.001;

        /* These are parameters for the shutter control */
        N90_shutter=50; // This is the number of pulses required to turn the stepper motor about 90
        degrees.
        delay_sh=0.003;
    } while (0);
}
```

```

space_sh=0.001;
/* END shutter parameters */

begin();

/* Set the Frequency for Channel 1 and 2 */
sf= sf1+((double) sfloffset)/1e6;
set_freq1(sf);
set_freq2(sf2);

/* Amplitude and Phase need to be set on 1st use. */
EVENT d1 {PHASE1,phase0[acqn%8]} {RF1_BLNK,1} {AMP1,0.0} ;
//This should latch the phase output

/* BEGIN Pre-Sat sequence. Npresat_pul = number of pre-sat pulses */
for (i=0 ; (i < Npresat_pul) ; i++) {
    EVENT pw1 { RF1, 1} {RF1_BLNK,1} {AMP1,1.} {PHASE1,phase0[acqn%8]};
    EVENT presat_gap {RF1_BLNK,1};
}
/* END Pre-Sat Sequence */

/* BEGIN Shutter Control Sequence */
EVENT space_sh {BNC_1,0};
for (i=0 ; (i < N90_shutter) ; i++) {
    EVENT delay_sh {BNC_0,1},{BNC_1,0};
    EVENT space_sh {BNC_1,0};
} //turnshutter 90deg

/* EVENT tau-shutter-2*((N90_shutter+1)*(delay_sh+space_sh)); */
/* This is a rough measure of delay, not as good as above probably, but more understandable
*/
EVENT tau_1;

EVENT space_sh {BNC_1,1};
for (i=0;i<N90_shutter;i++) {
    EVENT delay_sh {BNC_0,1},{BNC_1,1};
    EVENT space_sh {BNC_1,1};
} //turn back shutter 90deg

/* This is the delay to wait after light is off before acquisition */
EVENT tau_d;
/* END Shutter Control Sequence */

/* BEGIN MAIN PULSE SEQUENCE */
EVENT pw2 { RF1, 1} {RF1_BLNK,1} {PHASE1,phase1[acqn%8]} {AMP1,1.0};
EVENT rd {AMP1,0.0};
/* END MAIN PULSE SEQUENCE */

/* Data Acquisition Sequence */
/* Usually don't have to modify */
SYNC_DSP;
EVENT get_dwell()*get_npts() {AD_STAQ,1} {RCVR_GATE,1};

/* This is the delay between multiple acquisitions (for averaging) */
/* Usually don't have to modify this */
EVENT PPO {PP_OVER, 1};

} while( ready( ph_rec[acqn%8] ) == P_PROGRAM_CALC );

done();
return 0;
}

```


Appendix J. Fundamental constants and other values

This section contains the value of fundamental constants and other constants which were used in the numerical calculations. The majority of the fundamental constants can be obtained from the National Institute of Standards and Technology (NIST), which is available on-line at <http://physics.nist.gov/cuu/Constants/>.

Table 7 : Fundamental constants and other useful values

<i>Symbol</i>	<i>Description</i>	<i>Value</i>	<i>Units</i>
k	Boltzmann's constant	$1.3806505 \times 10^{-23}$	J K ⁻¹
		8.617343×10^{-5}	eV K ⁻¹
		2.0836644×10^{10}	Hz K ⁻¹
h	Planck's constant	$6.6260693 \times 10^{-34}$	J s
		$4.13566743 \times 10^{-15}$	eV s
ħ	h/2π	$1.05457168 \times 10^{-34}$	J s
		$6.58211915 \times 10^{-16}$	eV s
γ _p	proton gyromagnetic ratio	2.67522205×10^8	s ⁻¹ T ⁻¹
		42.5774813	MHz T ⁻¹
γ _e	electron gyromagnetic ratio	$1.76085974 \times 10^{11}$	s ⁻¹ T ⁻¹
		28024.9532	MHz T ⁻¹
γ(¹¹¹ Cd)	¹¹¹ Cd frequency relative to ¹ H at 100	21.215480	-
γ(¹¹³ Cd)	¹¹³ Cd frequency relative to ¹ H at 100	22.193175	-
γ(¹²³ Te)	¹²³ Te frequency relative to ¹ H at 100	26.169742	-
γ(¹²⁵ Te)	¹²⁵ Te frequency relative to ¹ H at 100	31.549769	-

B

bandgap, 17, 23

bandgap of CdTe, 23

C

carrier concentration, 17, 48

cryostat, 18

E

electronic g-factor, 24

F

fundamental constants, 73

I

irradiation time, 34

M

mobility, 17

N

NMR coil, 44

P

polytypism, 25

R

resistivity, 48

S

spin diffusion, 28

spin temperature, 28

T

temperature controller, 18

tip angle, 19

W

wavelength meter, 18