Nuclear Magnetic Resonance Study of Three Dimensional Dirac Semimetal Na$_3$Bi

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Abstract

Dirac semimetals (DS) possess promising electrical characteristics because the shape of their electron band structure allows some electrons to behave as massless particles, resulting in high conductivity. Of particular interest are the three-dimensional Dirac semimetals, where this interesting band structure is present along all three dimensions. In this paper, we attempt to probe the local conditions of a three-dimensional Dirac semimetal, Na$_3$Bi, using nuclear magnetic resonance (NMR). This material has three distinct nuclei sites within the crystal lattice. Studying each of these sites using NMR can provide insight into the interactions among the nuclei and between the nuclei and the surrounding electrons. Na$_3$Bi has a complex NMR spectrum which requires further study to understand.

Na$_3$Bi as a Dirac Semimetal

Two-dimensional Dirac semimetals, such as graphene, are a hot topic of research in topological materials because of their unique electronic properties and potential in electronic applications. The electron band structure of ordinary semimetals differ from insulators and conductors as the top of the valence band and bottom of the conduction band have a small overlap. In Dirac Semimetals (DS), these bands touch only at discrete points, known as Dirac points. At these Dirac points, electrons have a linear dispersion relationship, forming 'Dirac cones.' The dispersion relationship is the relationship between the energy and the momentum of a particle. Free electrons have a parabolic dispersion relationship but massless particles, like photons, have a linear dispersion realationship. The linear dispersion relationship in Dirac semimetals allows electrons close to the Dirac points to behave as massless particles (Dirac fermions).[1-4, 6] This gives graphene its unique electronic properties.

Unfortunately, graphene cannot easily be studied using nuclear magnetic resonance techniques. NMR requires a large sample ($\sim 10^{23}$) of nuclei with non-zero spin. The thin sheets of graphene provide a small sample size of carbon atoms, most of which have nuclei of spin zero. Of the naturally occurring carbon isotopes, only the 1.1% naturally abundant carbon-13 nuclei have a non-zero spin. While it is possible to produce a graphene sheet exclusively with ^{13}C, this method is expensive and the small sample size may still yield too weak of an NMR signal for measurements.

NMR techniques may still be useful to probe the internal electric and magnetic structure of other DS. Of particular interest are the three-dimensional Dirac semimetals in which the relationship of energy to momentum disperses linearly along all three momentum directions, forming bulk Dirac fermions.[1,2] Figure 1 A shows Dirac cones in the dispersion relation of 3D DS Cd$_3$As. Although these materials are similar to topological insulators and two-dimensional Dirac semimetals, they have the unique property of high electron mobility and conductivity in all three dimensions. Because 3D DS are a neighbor material to various quantum states, their study may yield to the realization of other novel states.[3] In addition, 3d DS also exhibit many complex quantum properties.

The 3D DS, Na$_3$Bi has a hexagonal crystal lattice with two sodium sites, Na(1) and Na(2), and a single bismuth site. Na(1) and Bi form honeycomb layers stacked along the c-axis with Na(2) connecting the layers at the bismuth site.[1] Figure 1 B shows a single unit cell of Na$_3$Bi. The large yellow spheres represent sodium sites 1 and 2, with Na(1) bonded to the bismuth atoms in planes and Na(2) connecting layers between the bismuth sites. The smaller purple spheres represent bismuth atoms. Sodium-23 and bismuth-209 are
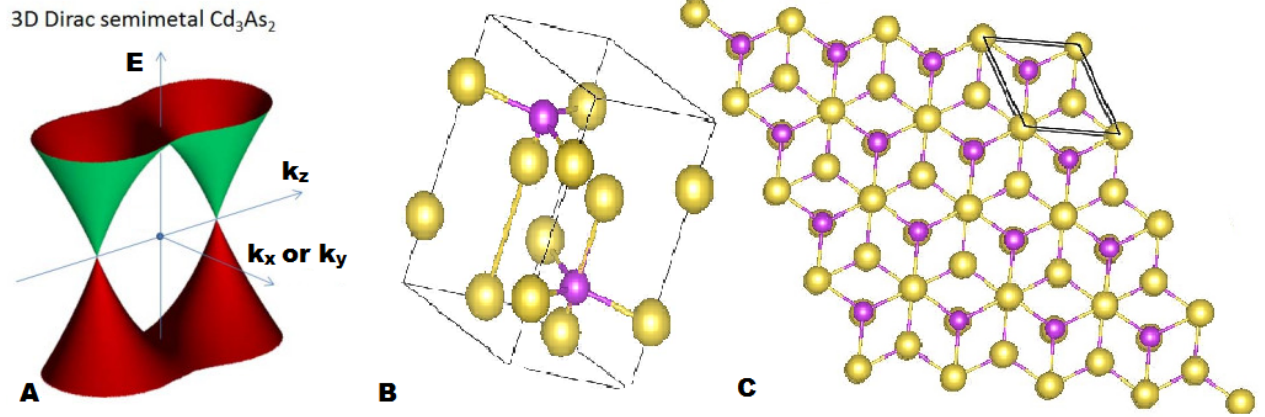
Figure 1: **A** Dispersion Relation of a 3D Dirac Semimetal with two Dirac points.[7] **B** A single unit cell of Na_3Bi. Sodium atoms are shown in yellow and bismuth is shown in purple.[8] **C** A hexagonal plane of Na_3Bi where the c-axis is coming out of the paper. A single unit cell is outlined.[8]

both 100% naturally abundant nuclei with non-zero spin making Na_3Bi a good candidate for NMR study. Because there are two sodium sites with different symmetries, it is possible to obtain two separate signals from sodium, as well as a signal from bismuth.

NMR and Experimental Techniques

Nuclear magnetic resonance is a powerful technique used to probe a material's internal conditions through the behavior of the nuclear spins as they interact with an external magnetic field, spins of local nuclei, electron spins and the local electric field. These various interactions can be expressed in terms of the nuclear spin Hamiltonian:

$$H = H_z + H_{dip} + H_{hyp} + H_Q$$

where H_z is the Zeeman interaction, H_{dip} is the dipole interaction, H_{hyp} is the hyperfine interaction, and H_Q is the quadrupole interaction.[9]

The Zeeman interaction describes the energy of a nuclear magnetic moment in a magnetic field and can be written as:

$$H_z = \mu \cdot H_0$$
$$= \gamma \hbar \hat{I} \cdot H_0$$

where μ is the magnetic moment of the nuclei, H_0 is the applied magnetic field, $\hbar$ is Planck's constant divided by 2π and $\hat{I}$ is the nuclear spin operator. γ is the ratio of the magnetic dipole moment to angular momentum, or the gyromagnetic ratio, and is a value unique to each isotope. The Larmor frequency, ω_L can be defined as:

$$\omega_L = \gamma H$$

Where H is the magnetic field at the nuclei. If we ignore the interactions between the nucleus, electrons and other nuclei, H becomes H_0. The Zeeman interaction can now be re-written as:

$$H_z = \hbar \omega_L \hat{I}_z$$

This equation has energy eigenvalues $E_m = \hbar \omega_L m$, where $m = \pm 1/2$ for a spin 1/2 nucleus. When $H_0 = 0$, the nuclei's spin states are degenerate but energy level splitting with $\Delta E = \hbar \omega_L$ occurs when a field is applied.[10] Nuclei can transition between levels by emitting or absorbing a photon with energy $\hbar \omega_L$.
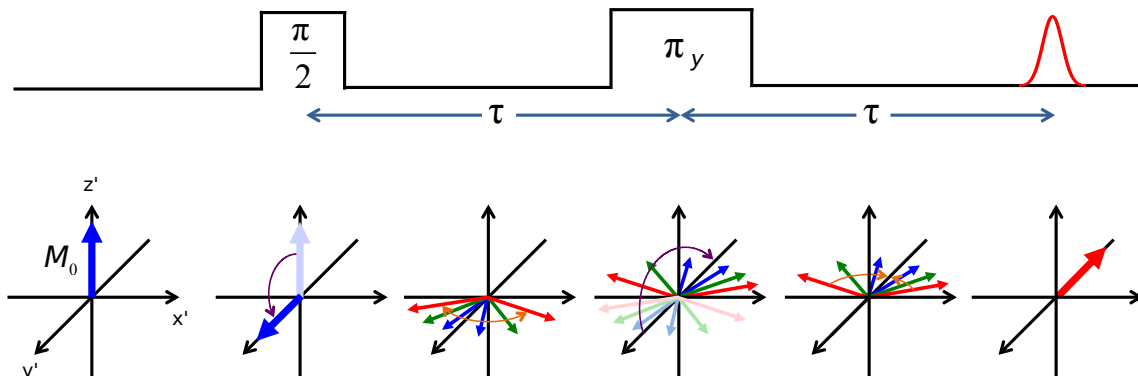
Figure 2: The complete Hahn echo sequence: The unperturbed spins are initially aligned in the direction of the magnetic field (M_0). An RF pulse flips the spins $\pi/2$ radians, causing them to precess at different rates in the x'y' plane. A second pulse flips the spins π radians but does not change the angular velocity of the precessions. When the spins re-align, the RF coil reads the NMR signal. The amount of time, τ, from the initial pulse to the second is equivalent to the time from the second pulse to the measured signal.

While the Zeeman interaction describes a lone nuclear spin with an applied external field and is the largest contributing factor to the nuclear spin Hamiltonian, H, it is important to understand the hyperfine, dipole, and quadrupole interactions when studying condensed matter systems. The hyperfine interaction, H_f, describes the interaction of the nuclei with the spins of the surrounding electrons. H_{dip}, the dipolar interaction, is the interaction of the nucleus spin with its neighboring nuclei. Nuclei of spin greater than $1/2$ also interact with the local electric field gradient, called the quadrupole interaction, H_{quad}.[9]

Typical NMR experiments consist of a radiofrequency (RF) coil wrapped around about 10^{23} nuclei with non-zero spin inside of a magnetic field. The RF coil generates an oscillating electromagnetic (EM) field. To maximize signal, it is important that the coil is wrapped as closely around the sample as possible. For this reason, a new coil is used for each sample measured in this paper. In a basic pulse measurement, the frequency generated by the RF coil is used to excite the spin states of the nuclei. When the spins relax back into equilibrium the coil measures the signal. This method yields a poor signal-to-noise ratio and modern NMR techniques use a spin echo sequence instead.

In our experiments, we used a Hahn echo sequence. The RF coil emits a pulse long enough to knock the nuclei spins over $\pi/2$ radians, from the z'-axis to the x'y' plane, in the reference frame rotating at the Larmor frequency. The spins then begin to precess about the direction of the magnetic field. Due to the different positions of the nuclei in the material and thus the different interactions between each nucleus and its neighbor, the spins precess at different rates, causing them to spread out. The RF coil then emits a second pulse, twice as long as the first, to flip the spins π radians. The spins continue to precess at the same rates in the same direction, but are now precessing toward each other rather than away. Although the spins have spread out, they continue with their same initial speed and will all re-align at the same time. When they re-align, the coil reads in the full signal emitted. The full Hahn echo sequence is illustrated in Figure 2. The process is analogous to racers on a track: the racers begin at an initial starting line. When the signal is given, they begin running at different speeds. If, after some amount of time, they are given a second signal to turn around and run back, even though the faster runners have crossed a farther distance than others, they will all reach the start line at the same time, assuming their speed does not change. This sequence can be repeated many times and the signal averaged to reduce noise.

NMR spectra can be obtained by either sweeping the external magnetic field while the frequency of oscillation of the EM field remains constant or sweeping the frequency at a constant magnetic field.[10] These field or frequency sweeps reveal the locations of spins in field and frequency space. Nuclei that are only subject to the Zeeman interaction will resonate at $\omega_L = \gamma H_0$. In a correlated system, this resonance may shift as a result of other interactions. The NMR spectrum of a material will show these shifts and give insight into how the nuclei interact with their environment. For a nuclei of spin $1/2$, there is a single resonance
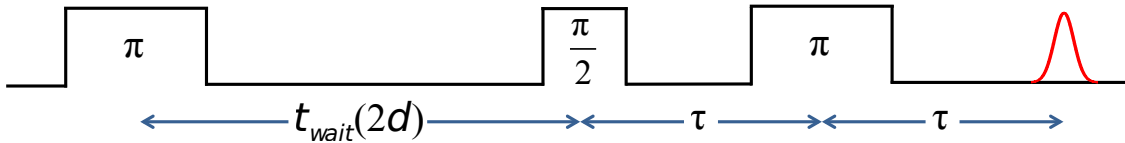
Figure 3: T1 measurement sequence: An RF pulse is applied to flip the spins π radians. The spins are allowed to relax for some variable amount of time, t_{wait} before the spins are perturbed in the Hahn Echo Sequence.

line at the Larmor frequency. Sodium has a spin $3/2$; therefore, for a single sodium site there can be three resonance lines (a central peak and two satellites). Bismuth has a spin of $9/2$ and can have nine separate resonance lines. This effect is due to the quadrupole interaction. Because Na_3Bi has two sodium sites with different symmetries, a complete NMR spectrum may have two sets of three resonance lines from each of the sodium sites and one set of nine resonance lines from the bismuth atoms.

The resonance lines can be further characterized with spin-lattice-relaxation time, T_1 measurements. T_1 is the characteristic relaxation time, or the amount of time it takes for perturbed pulses to relax back into equilibrium. This value varies depending on the nuclei spin number, the peak measured, and the material. Metals have a short relaxation time ($<< 1s$) while the spin relaxation of an insulator can take several minutes. The T_1 measurements performed here consist of a short RF pulse to flip the spins pi radians, a variable amount of time, t_{wait}, during which the spins may begin to relax, and a Hahn Echo Sequence (see figure 3). The signal response over t_{wait} can be fit to a function of the form $1 - exp(-t_{wait}/T_1)$. This formula varies depending on the spin number of the nuclei and the peak measured. T_1 and its temperature dependence may be useful for understanding the material, the interactions of nuclei and interpreting the signal measured by its spin number.

Two samples of Na_3Bi were measured in a Physical Property Measurement System (PPMS) magnet with a maximum field of 9 Tesla. The samples were mounted with the c-axis parallel to the magnetic field and a copper RF coil was wound tightly around both the sample and the platfom. The samples were oriented inside the PPMS such that the EM field from the copper coil was perpendicular to the magnetic field and the c-axis. Because Na_3Bi is extremely air sensitive, both samples had signs of external oxidation. NMR is a bulk measurement technique and oxidation that is only on the surface should not have a strong enough signal to affect the data. Sample 1 was visibly more oxidized and slowly degraded even once inside the magnet. Although we were able to take data over a period of several days, some of the resonance lines disappeared as the sample degraded. This is a result of the surface oxidation seeping in throughout the crystal, creating sodium oxide. To prevent the further degradation of Sample 2, it was epoxied in a glove box and covered with a second layer of vacuum grease.

Results and Future Work

The samples show at least three main Na lines in the NMR spectrum. Figure 4 shows a field sweep NMR spectrum of both samples obtained at the same frequency and temperature. The central line's location in field and frequency space is not shifted from the central line in pure sodium. Each of the three sodium groups in the first sample have three separate lines. More detailed sweeps of the smaller groups(groups 1 and 2), which are symmetric about the large Na line, reveal a double-peaked behavior (see Figure 5 A). After sample 1 had degraded, the smaller sodium sites could no longer be measured while the central line remained in the same frequency and field position without change. Sample 2 has none of the triplet or double-peaked behavior, though the two smaller peaks are also symmetric about the central line. There is another signal located at about 5.548T and may be a second new signal that is obscured by copper line. These two signals are symmetric about the central sodium resonance and should be investigated further. The differences between samples 1 and 2 may be a result of oxidation of sample 1, sample orientation or crystal impurities. This can be determined by performing angular-dependent measurements and conducting
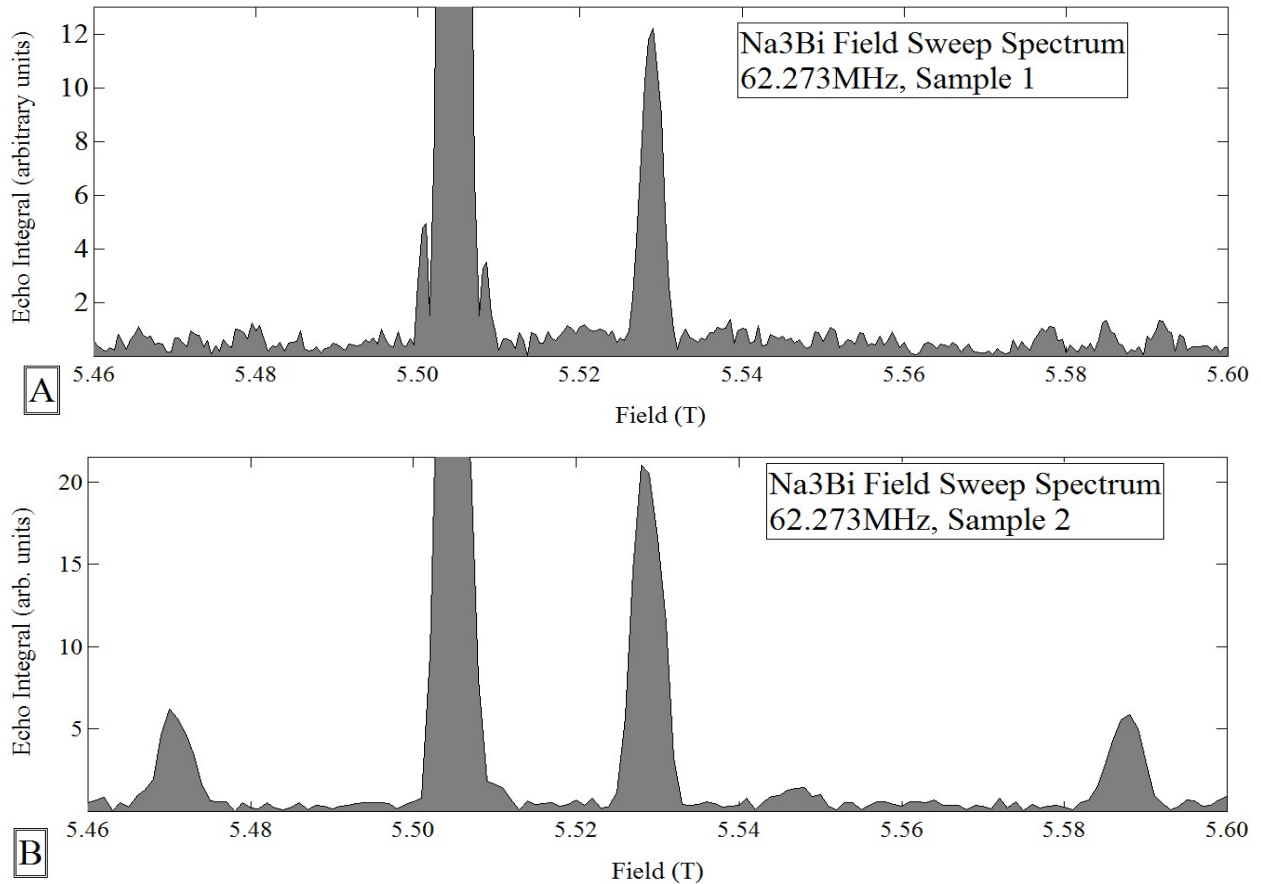
Figure 4: Field sweep spectrum of Na_3Bi, Samples 1 and 2 at 62.273MHz and 250K. The large peak located from 5.5 to 5.51T is the copper of the RF coil and can be ignored. The central Sodium line is at 5.53T with the two smaller Sodium lines symmetric about the central line at around 5.47T (Group 1) and 5.588T(Group2). **A** Sample 1: Each of the Sodium lines are sets of triplets. The two smaller sites also have a double peak behavior visible in Figure 5 A. **B** Sample 2: The Sodium lines do not show the same triplet or double peak behavior as in sample 1. There is another Sodium signal at 5.548T

more measurements on new samples.

Multiple field and frequency sweeps reveal that groups 1 and 2 move linearly in field and frequency space. Figure 5 B shows the linear relationship between frequency and field of sample 1, groups 1 and 2. The double peak behavior of the triplet groups was visible in each frequency and field sweep. To identify the sodium peaks, T_1 measurements were performed on the central resonance line. Figure 6 shows the data from these measurements with a line of best fit. The data fit well to the function describing the central resonance line of nuclei with spin 3/2. This suggests that this central line may be the Na nuclei at one of the two sodium sites in Na_3Bi, rather than the sodium that was corrupted by oxidation, as we originally suspected. The strength of this peak in sample 2 further indicates that this resonance line is significant to Na_3Bi. The T_1 of this line is about 3.7s. This is a typical T_1 for a semimetal. It is possible that the central line and groups 1 and 2 are only the resonances of one of the sodium sites in Na_3Bi. More field sweeps should be conducted to search for another sodium site and further T_1 measurements of the other sodium resonances can be conducted to determine the nature of these peaks. Temperature-dependent T_1 measurements will also give insight into the correlation of the nuclei.

Recent field sweeps have revealed a resonance line of bismuth although many more measurements need to be taken. Because bismuth is a quadrupole nucleus of spin 9/2, there may be as many as eight other resonance lines, or this single line measured may be a combination of all nine lines. This should be examined
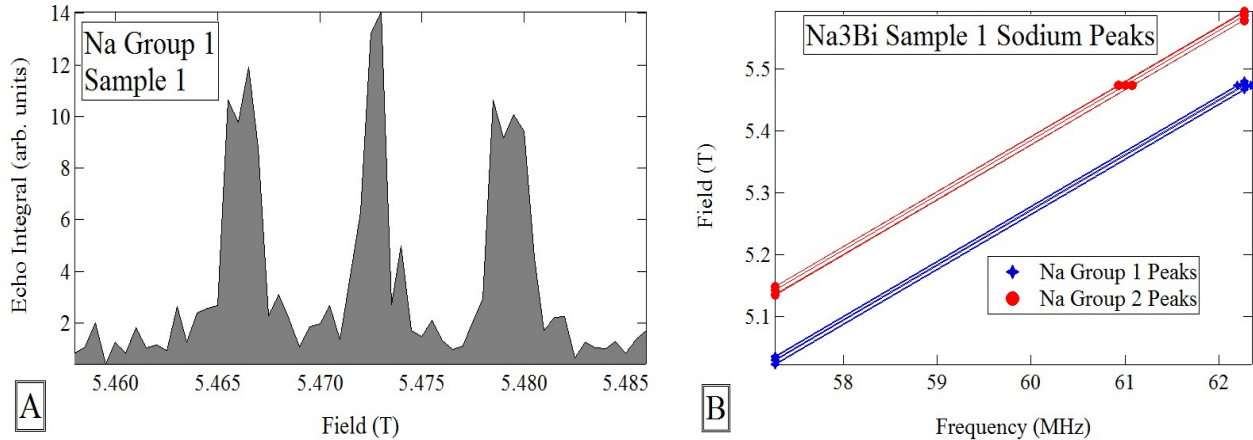
Figure 5: **A** Greater resolution field sweep of sodium group 1, sample 1 at a frequency of 62.273 MHz and a temperature of 250K. The sodium lines at about 5.465T and 5.48T reveal a clear double peak behavior. There may also be two peaks in the central line. A field sweep of sodium group 2 revealed a similar behavior. Three lines with double peaks was a behavior consistent throughout all field and frequency sweeps of these sodium groups in this sample. In sample 2, the same sodium groups are single lines lacking both the triple line behavior and the double peaks visible here. **B** The location of the triple peaks of sodium groups 1 and 2, sample 1 from several field and frequency sweeps. The peaks move linearly across field and frequency space for both groups.

by maximizing the signal to noise ratio at this peak and then performing more frequency or field sweeps to look for the other peaks. T_1 measurements can also be useful for studying the bismuth site and determining which resonance line is seen.

Na$_3$Bi may have much more interesting features in its NMR spectrum so further field and frequency sweeps should be conducted. The measurements included in this paper were done at a temperature of 250K; however, this material may have interesting behaviors that should be studied at other temperatures. These results show that nuclear magnetic resonance can be used to study the internal electronic and magnetic behaviors of a Dirac semimetal. Na$_3$Bi has a complex NMR spectrum that should be studied in depth. Further studies are needed before much can be said about NMR in Na$_3$Bi.

Acknowledgments

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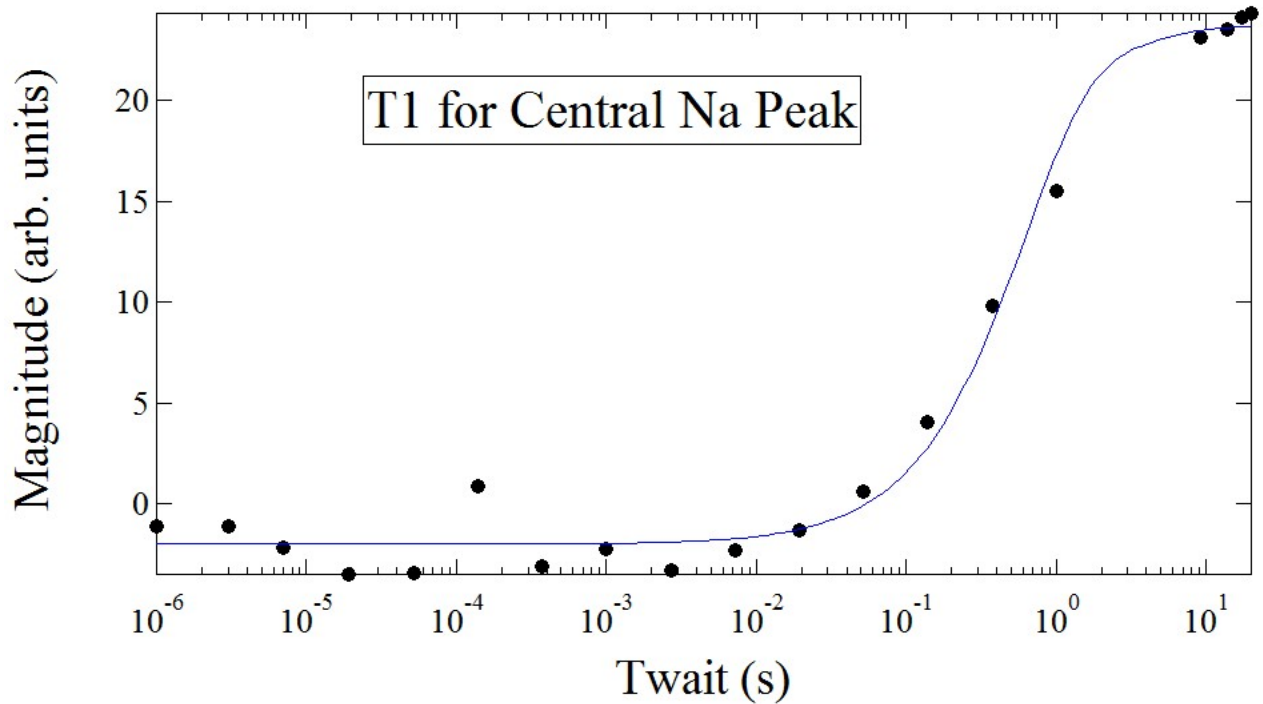
Figure 6: T_1 measurement performed on the central sodium line of sample 2 at 250K. The data fit most closely to the central resonance line of a nucleus with spin 3/2. The T_1 of this resonance line was approximately 3.7s.

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