

# NMR INVESTIGATIONS OF HELIUM-3 ADSORBED ON BORON NITRIDE

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## ABSTRACT

Pulse nuclear magnetic resonance technique (NMR) was used to study the two dimensional system of  $^3\text{He}$  adsorbed on Boron Nitride (BN). The spin-lattice relaxation time was found to be a linear function of frequency for low coverage data, while an exponential behavior was observed for high coverage one. Temperature dependence of both spin-lattice relaxation time  $T_1$  and spin-spin relaxation time  $T_2$  show a maximum value around 2 K which is unusual behavior for 2-d system. This behavior indicates two different relaxation mechanisms of the system.  $T_1$  was found to have minima around 0.85 monolayer for a range of Larmor frequency extends between 1 and 10 MHz. On the other hand,  $T_2$  decreases to approach zero near the monolayer completion as reported for helium-3 adsorbed on grafoil.

## INTRODUCTION

Grafoil is a favorable substrate to study the physisorption phenomena. It was used successfully as an absorber for  $^3\text{He}$  atoms which are considered as adsorbent. Although lots of work has been made on grafoil [1,2,3]; problems were raised up due to the magnetic and electrical properties of graphite. Previous NMR adsorption on grafoil [4] show that the magnetic and electrical properties of graphite greatly determine the observed relaxation times. This is due to the unusual large anisotropic susceptibility of graphite ( $1.7 \times 10^{-5}$  emu/gm) which produces large magnetic field gradient in the voids between the grafoil platelets when the sample is placed in an external magnetic field. In addition to this magnetic behavior, there are also the electrical properties of graphite that should be considered. Grafoil is a conductor across its basal planes and special care must be taken in the construction of the sample chamber for r.f. shielding problems and for eddy current which heat up the sample during the application of the r.f. pulses. Considering these problems; an alternative substrate for NMR adsorption studies should be examined.

Early physical adsorption studies [5] have indicated a similarity between the adsorption isotherms of inert gases on graphite and Boron Nitride. Such a comparison is demonstrated by Matecki et al 1972 [6] for NO on both Boron Nitride and graphite at 78.3 K. This is due to the similarity between the structures of the hexagonal form of Boron Nitride and graphite.

Both materials have layer structure which account for their solid lubricant qualities. Hence the decision was made to use the BN as a substrate to study the  $^3\text{He}$  adsorption in the present work.

Boron Nitride is available as a white powder material, then it has the disadvantage of randomly oriented surface. Our sample has the average size particle of 50 microns. BN is an electrical insulator [7], so it does not present r.f. heating problems. BN is also diamagnetic material like graphite, but its magnetic susceptibility is two orders of magnitude smaller than that of graphite which is about  $4.8 \cdot 10^{-7}$  emu/gm [8]. Thus in general BN is considered a successful substrate.

## EXPERIMENTAL DETAILS

Two sample chambers were used. The first sample chamber was constructed from stycast 1266 in cylindrical shape of one cubic inch. The NMR coil directly wound onto the cell to improve the filling factor. This coil was made up of 7 copper strands and had 17 turns, its length was 33 mm as well as its diameter. The coil inductance was  $6.8 \mu\text{H}$  and the quality factor was 200 at helium temperature. The sample was heat treated in vacuum inside a stainless steel holder to remove gaseous paramagnetic impurities such as oxygen and water. An amount of boron nitride

of 9.45 gm was packed into the cell and sealed up in order to reduce the dead volume. An adsorption isotherm at 4.2 K was made, Figure (1), and the monolayer completion was estimated at  $23.5 \text{ cm}^3 \text{ STP}$ .

During the accumulation of data it was discovered that the sample had been contaminated with impurities coming out from the stainless steel holder during the heat treatment.

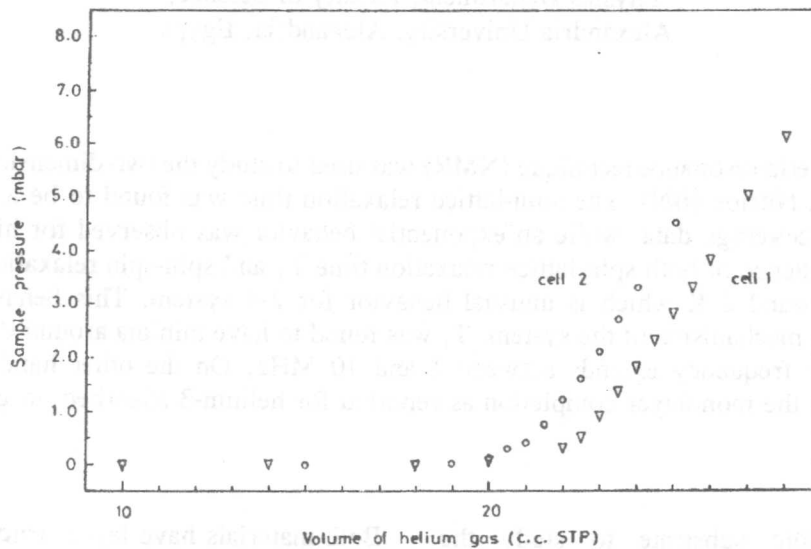


Figure 1. Helium-3 adsorption isotherm on BN at 4.2 K.

Table 1. Spectroscopic analysis (in ppm) of the BN sample before and after heat treatment.

element	unheated (ppm)	heated (ppm)	element	unheated (ppm)	heated (ppm)
Silver (Ag)	< 1	< 1	Mercury (Hg)	< 1	< 1
Gold (Au)	< 1	< 1	Magnesium (Mg)	10	3
Aluminum (Al)	30	50	Manganees (Mn)	3	100
Bismuth (Bi)	< 1	< 1	Molybdenum (Mo)	< 1	< 1
Calcium (Ca)	< 1	~ 5	Nickel (Ni)	< 1	< 1
Cobalt (Co)	< 1	< 1	Lead (Pb)	< 1	< 1
Chromium (Cr)	< 1	50	Antimony (Sb)	< 1	< 1
Copper (Cu)	< 1	< 1	Silicon (Si)	~ 200	~ 300
Iron (Fe)	~ 2	~ 100	Zinc (Zn)	< 1	< 1

A spectroscopic analysis before and after heat treatment shows these contaminations as in Table (1). To avoid these impurities, a second sample chamber was constructed. The sample was of the same shape and dimensions as the previous one. A similar NMR coil was established. This time, the sample was heated inside a large borosilicate closed tube, which is closed at both ends with grafoil foil. The quantity of packed sample was 9.13 gm resulted in a monolayer completion at 22.5 cm<sup>3</sup> STP as shown from the adsorption isotherm in Figure (1) using point B criterion.

A conventional dilution <sup>4</sup>He refrigerator was used. The master oscillator used is model 5600 Rockland frequency synthesizer with excellent stability and low noise. The minimum frequency available is 0.1 MHz and the maximum is 160 MHz. The pulse programmer used is a digital pulse sequence generator built in the laboratory [1]. The pulse width could be varied from 1 μsec to 9900 μsec in steps of 1 μsec. The delay changes between 10 μsec and 9900 m sec while the repetition time changes between 100 μsec and 9900 m sec in 100 μsec steps.

The super conductor magnet with its current control unit was provided by Oxford Instruments for a maximum field of 2 Tesla. The probe was a single parallel tuned NMR coil with a natural frequency of about 5 MHz. The matching and tuning unit at the top of the cryostat enabled the change of nominal frequency of the probe to higher or lower values (1 to 10 MHz) by connecting parallel conductance or capacitor respectively.

The measurements were all done at temperature of 1.2 K and they are classified as follows:

- $T_1$  was determined as a function of frequency for a range of coverage between  $x=0.55$  and 0.95 monolayer.
- $T_1$  was measured at a wide range of frequency; 1.29, 2.72, 3.73, 4.72, 5.72, 7.02, 8.72 and 10.87 MHz for the high density coverage between 0.7 and 1 monolayer. While  $T_2$  was monitored at one frequency only (5 MHz) to compare the behavior with that of <sup>3</sup>He adsorbed on grafoil for coverage up to monolayer completion.
- Temperature dependence of  $T_1$  was determined at frequency of 4.72 MHz for coverages  $x = 0.82, 0.84$  and 0.86 monolayer.

While that of  $T_2$  for  $x = 0.84$  and 0.86 monolayer.

## RESULTS AND DISCUSSIONS

### a. Frequency Dependence:

The frequency dependence of the longitudinal relaxation time  $T_1$  was measured at 1.2 K for various fractions of monolayer.

For intermediate coverage, around 0.55, a linear behavior was observed as in Figure (2). This linearity was found to obey the empirical formula;

$$T_1 = 3.8 \cdot 10^{-9} \omega_0$$

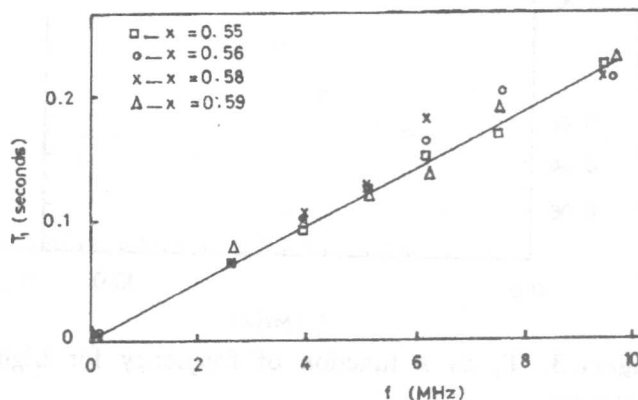


Figure 2.  $T_1$  as a function of frequency for low coverage.

This relation gives an indication that the longitudinal relaxation is mainly due to the motion of the spins in the magnetic field. The slope was found to be constant and independent of coverage. This behavior was observed in vycor glass as well [9]. The observation of the  $T_1$  linear dependence has been reported for <sup>3</sup>He adsorbed on various polycrystalline substrate [10]. However, although this behavior seems to be universal for these two dimensional systems, there is no general model which explains it satisfactorily for all frequency ranges observed.

For higher density coverages, an exponential relation is more compatible with the experimental data as shown in Figure (3) for coverages of 0.74 and 0.82 monolayer. The fitted expression is of the form,

$$T_1^{-1} = T_1^{-1}(0) \exp\left(\frac{-f_0}{f_{scale}}\right)$$

an Arrhenius relation with temperature,

$$T_{1,2} = A \exp\left(-\frac{E}{KT}\right)$$

Obviously, at low temperature,  $T_1$  displays the temperature independent quantum motion of the relaxation mechanisms as shown in Figure (4).

A maximum in  $T_1$  and  $T_2$  temperature dependence is an unusual behavior for a single relaxation process. Hence, it may be that two different mechanisms are responsible of the relaxation below and above the maximum. Above 2 K, the film might be in a liquid state, where the dipolar contribution is small (long relaxation time) and mechanisms with shorter relaxation time prevail. The  $T_{1wall}$  relaxation mechanism where the atoms relax when encounter an impurity center is a possible candidate. These maxima points might be associated with the melting transition temperatures of two dimensional solid. At high temperature the film is in the fluid state and a non-dipolar mechanism dominates. As the temperature becomes lower, the motion of the spins decreases and  $T_1$  dipolar becomes shorter and when the film solidifies the dipolar interaction dominates decreasing  $T_1$  on cooling. The Arrhenius relation is usually an indication at low temperature that the motion of thermally activated defects is modulating the dipolar interaction between spins. The observed maxima are almost independent of coverage, ruling out the possibility that they coincide with the melting point which obviously depend on the density of the film.

### c. Coverage Dependence:

The temperature dependence of the spin-lattice relaxation time demonstrated in Figure (4) revealed that  $T_1$  is temperature independent at low temperature in the high frequency density film. This behavior indicates that the relaxation is modulated by quantum motion. These low temperature  $T_1$ , when plotted as a function of coverage, displays the familiar  $T_1$  minima as shown in Figure (6) for frequencies extends between 1 and 10 MHz. The values of those relaxation times at the minima are shorter than the corresponding ones for helium adsorbed on grafoil [13]. The reason may be attributed to the non dipolar origin of  $T_1$  in the case of boron nitride.

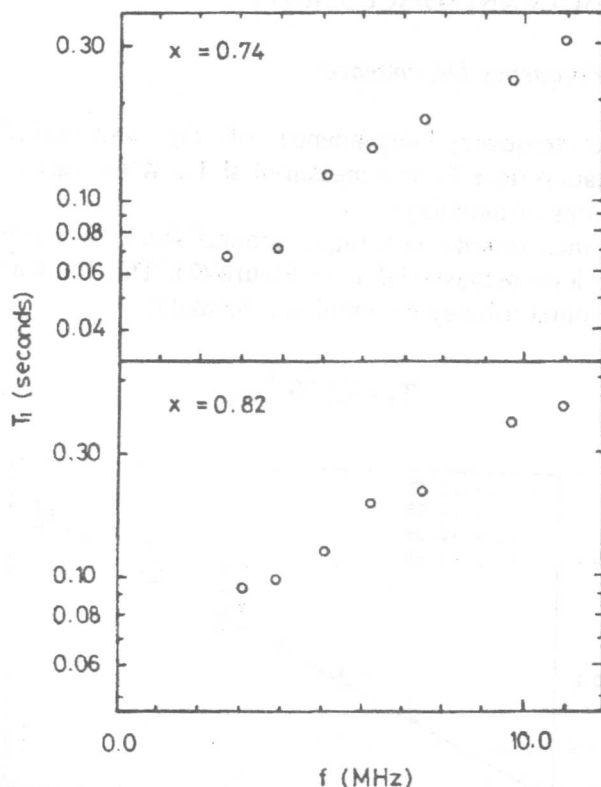


Figure 3.  $T_1$  as a function of frequency for high coverage.

In general, the dipolar spin-lattice relaxation time could be written as [11, 12];

$$\frac{1}{T_1} \approx \frac{1}{J} f\left(\frac{\omega}{J}\right)$$

where  $J$  is the characteristic frequency of the motion. This relation supports the belief that the origin of the relaxation mechanism is non-dipolar one.

### b. Temperature Dependence:

$T_1$  and  $T_2$  were determined as a function of temperature for a range of fraction of monolayer between 0.8 and 0.9. As shown in Figures (4), (5) both relaxation times exhibit a maximum with temperature, which is more pronounced for the former relaxation time. This maximum occurs at around 2 K. With decrease of temperature, both  $T_1$  and  $T_2$  follow

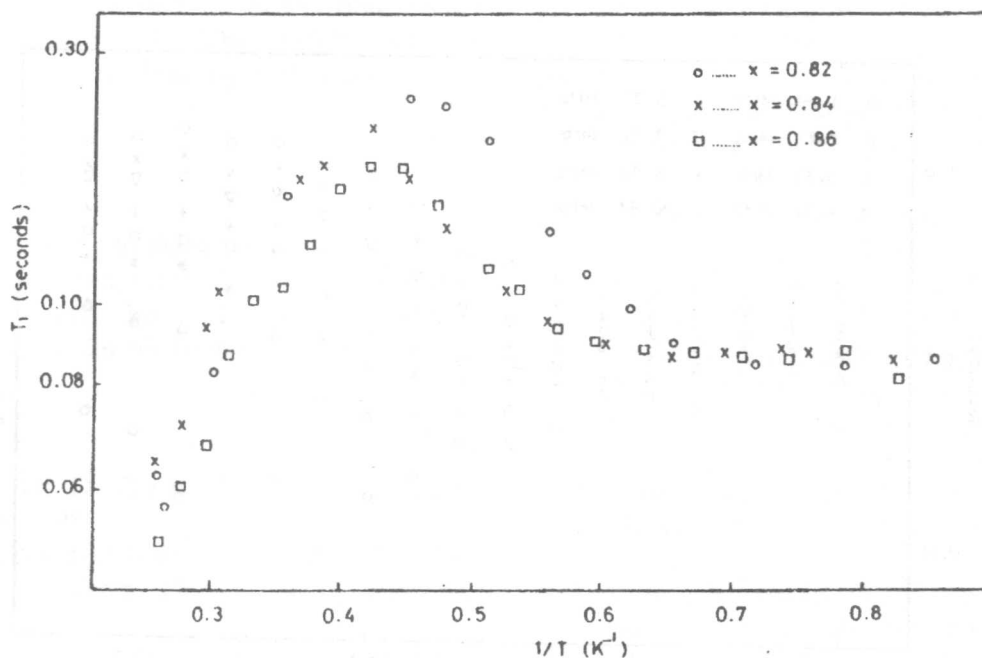


Figure 4.  $T_1$  as a function of inverse of temperature at  $x = 0.82, 0.84$  and  $0.86$  monolayer.

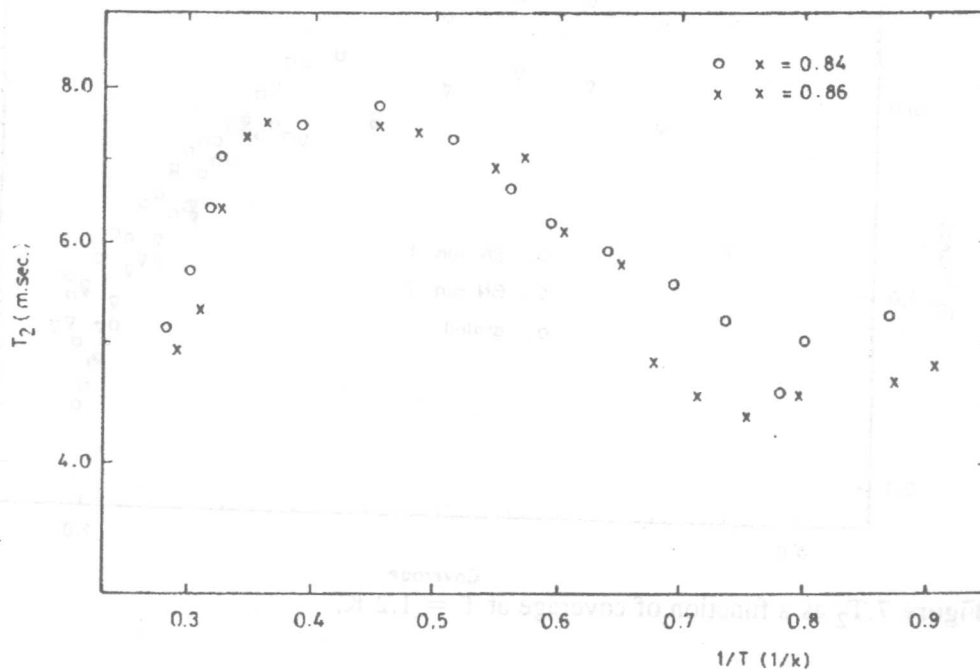


Figure 5.  $T_2$  as a function of inverse temperature at  $x = 0.84$  and  $0.86$  monolayer.

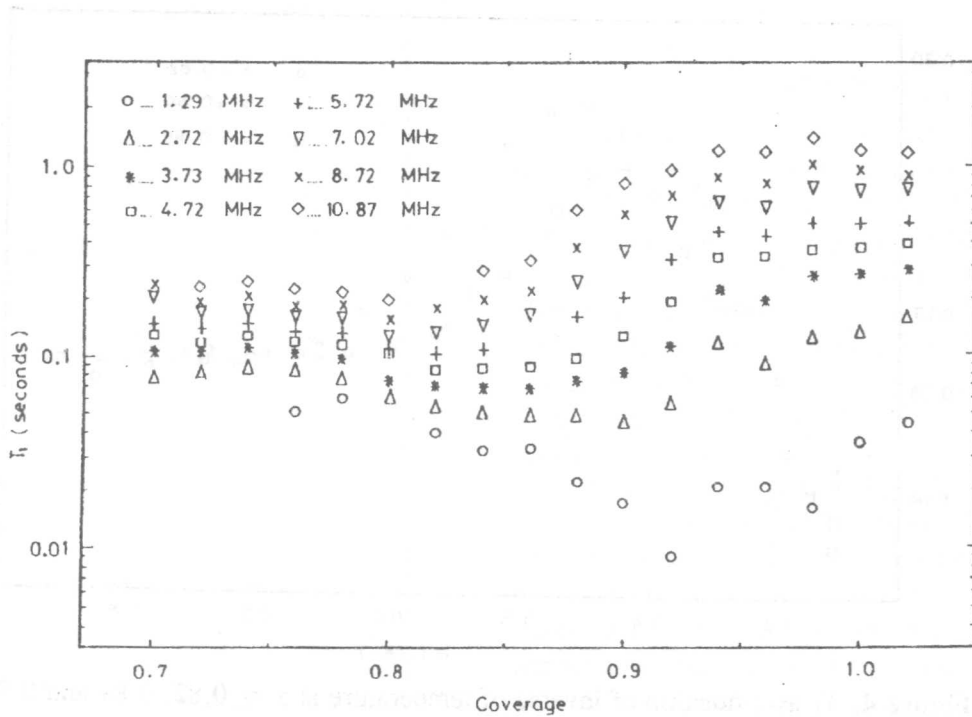


Figure 6.  $T_1$  as a function of coverage at  $T = 1.2$  K

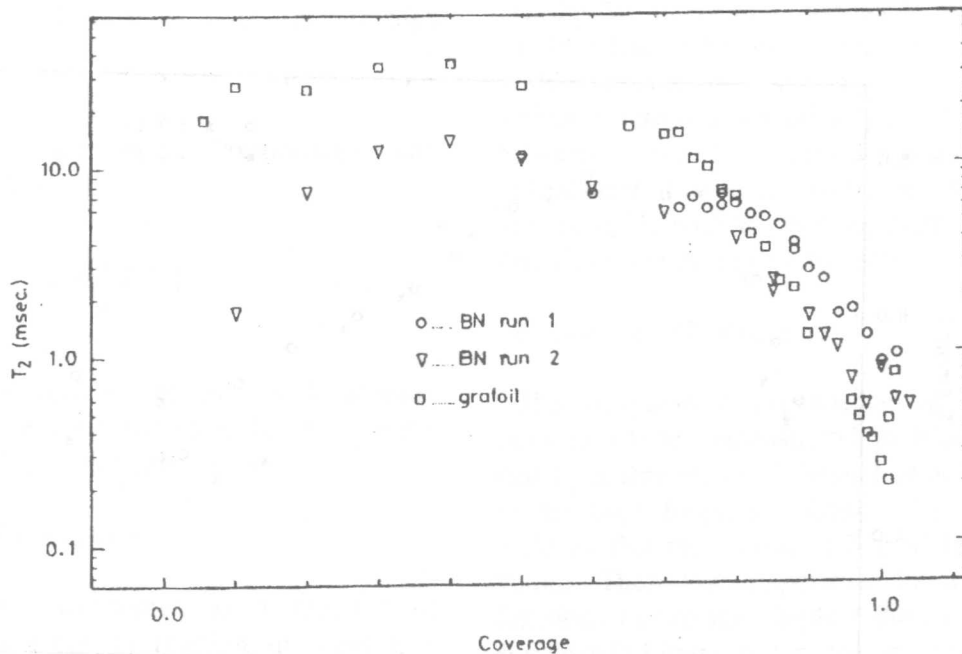


Figure 7.  $T_2$  as a function of coverage at  $T = 1.2$  K.

The  $T_2$  data displays some of the characteristics already encountered in the corresponding system of grafoil. As shown in Figure (7) for Larmor frequency

of 5.1 MHz, the data for both systems display the same behavior and the dipolar interactions prevails.  $T_2$  decreases to have a minimum at a monolayer



completion which is characteristic of tow dimensional homogeneous systems [14]. The grafoil data was obtained from the work done by both Kent [1] and Abulnasr [13].

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