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REDUCTION IN SMALL PARTICLES

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NUCLEAR SPIN-LATTICE RELAXATION REDUCTION IN SMALL PARTICLES

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Abstract

A method is described of reducing the nuclear spin-lattice relaxation time in a polycrystalline solid without the introduction of any paramagnetic impurities. It relies on the fact that the relaxation times of nuclei on a surface are usually much shorter than those in the bulk due to greater freedom of movement. Simply reducing the particle size by grinding or other methods is shown to be effective in markedly reducing the spin lattice relaxation time of all the nuclei in the specimen because of the good thermal contact between like nuclei in the interior and surface of small particles. The Nuclear Quadrupole Resonance (NQR) of ^{14}N , ^2D or ^{23}Na was measured for the same specimens with different particle sizes by nuclear quadrupole double resonance to ensure that the chemical structure of the compound did not alter due to the grinding. In all samples studied, except sodium thiosulphate the NQR spectrum was unaffected by the grinding except that the time necessary to collect the data was reduced. In the case of sodium thiosulphate a marked change in the NQR spectrum was observed despite the fact that no change in chemical composition could be detected. Data is presented which demonstrates the effectiveness of the technique and a simple model of the underlying mechanism is described.

INTRODUCTION

By prolonging unduly the time required for an experiment as a consequence of a long nuclear spin-lattice relaxation time T_1 of a sample may represent a great handicap in nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) and nuclear quadrupole double resonance (NQDR) experiments. The shortening of the T_1 by use of paramagnetic centres and paramagnetic impurities has been known since the early times of NMR^{1,2}. A very small concentration of paramagnetic centres is able to reduce the relaxation times by orders of magnitude. Bloembergen² proposed a theoretical model capable of explaining the process of relaxation in these systems. His model relies on the fact the nuclear spins close to the paramagnetic centres are in very good thermal contact with the lattice due to the presence of the fluctuating dipole field created by the paramagnetic centres. The spins far from these centres are indirectly coupled to the lattice by spin diffusion from the centres. Extensive experimental work was done in the past with impurity ions of the 3d group and rare-earth ions in a variety of crystals^{3,4,5} which support the basic ideas and approximations of Bloembergen's model.

In this paper an alternative method is proposed that does not contaminate the sample. It relies upon the rapid spin lattice relaxation found for nuclei on a surface and the coupling, through spin diffusion, between these nuclei and the other like nuclei in the specimen. Merely by reducing the grain size of a polycrystalline specimen by mechanical grinding or other methods, the effective spin lattice relaxation time of all the nuclear spins within the grains may be reduced.

EXPERIMENTAL AND RESULTS

The proton spin-lattice relaxation time T_1 in the large (0.7 T) applied field was measured by saturating the proton signal with a comb of 90° pulses and then monitoring

the recovery of the free induction decay. An estimate of the dipolar (zero field) spin lattice relaxation time T_{1D} was obtained by field cycling⁶ experiments in which the spin saturated specimen is rapidly transferred to a region of zero applied magnetic field for varying recovery times before being returned to the high field to monitor the free induction decay. The NQR spectra were measured by nuclear quadrupole double resonance (NQDR) which has been fully described elsewhere⁶ and will not be discussed again here.

The initial set of experiments were performed on finely divided frozen liquids. In the first, a stable emulsion of water droplets of diameter about 10^{-4} m in a matrix of n-heptane containing sorbitan tristearate (SPAN) was formed as described by Rasmussen and Mackenzie⁷. The relaxation times T_1 and T_{1D} of the ice 1h protons at 77K were two orders of magnitude shorter than those of identical ice in bulk specimens. The reduction was the same for slow and rapid cooling of the specimen. The deuterium NQR spectrum of ice in the frozen emulsion was identical to that in bulk ice, however, the spectrum could be obtained in several minutes rather than several hours.

The decrease in relaxation times cannot be ascribed to thermal contact between protons in water and those in heptane. The T_1 of the bulk ice used was about 600 seconds, that of the heptane was about 60 seconds while that of the ice protons in the emulsion was about 2 seconds. The T_{1D} of the bulk ice was longer than 30 seconds, however the T_{1D} of the heptane either in bulk or in the emulsion was too short to measure (i.e. less than about 1 second) using our method, and yet the T_{1D} of the ice protons in the emulsion was about 3 seconds. A feature of all these experiments with heterogeneous frozen specimens is that thermal contact between nuclear spins in adjacent but different phases is very poor.

A second set of experiments was performed with frozen liquids dispersed in solid powders at 77K. For example a quantity of γ -Al₂O₃ with particle size about 1.5×10^{-8} m was moistened with a solution of 50% H₂O mixed with 50% D₂O by weight. For a fixed

weight of Al_2O_3 the water mixture content was varied and the T_1 and T_{1D} of the water varied from both very short with little liquid to much longer times when the liquid content was increased. Similar results were obtained with water in Si_2O_3 and with other liquids such as formamide in both Al_2O_3 and Si_2O_3 . In all these cases the NQR spectra of the ^2D or ^{14}N nuclei were unchanged from those of the bulk sample.

A particularly clear demonstration of the effect may be obtained using a mixture of formamide and finely ground sodium chloride. If the mixture is frozen immediately after being vigorously agitated so that the solid particles are evenly distributed the T_1 of the protons in the formamide is reduced from the bulk value of about 600 seconds to a value of about 30 seconds. The same specimen is then warmed to room temperature and allowed to stand for 24 hours so that the salt precipitates to the bottom of the specimen tube. When the specimen is re-frozen the value of the proton T_1 in the formamide is close to its bulk value ruling out the possibility of chemical contamination of the formamide as the cause of the reduced T_1 in the dispersed specimen. In addition the reduction in the formamide proton T_1 for a dispersed sample is less if the salt particles are less finely ground.

INSERT TABLE 1

More quantitative results similar to these are shown in Table 1 in which some solid adsorbents were degassed at 600K under vacuum and then cooled and exposed to various pure adsorbates in the form of volatile liquids. The quantity of liquid adsorbed was determined by weight and the composite specimen quenched to 77K. It is seen that using the $\gamma - \text{Al}_2\text{O}_3$ with a particle size of 1.5×10^{-8} m in diameter marked reductions in the T_1 of the protons in the adsorbates are recorded when compared with their bulk values. Similar results are obtained with molecular sieve material as adsorbent.

The ^{14}N NQR spectra of these materials adsorbed on to the molecular sieve were compared with the NQR spectra of the same material in the bulk, these spectra appeared unaltered within the resolution of our technique. This again confirms that the reduction in T_1 of the material is due to the increase in ratio of molecules on the surface to those in the bulk. Since in these experiments all the liquids were outgassed using the freeze-pump-thaw method the possibility that the reduction in T_1 is caused by the presence of paramagnetic impurities, such as oxygen, on the surface of the material is excluded.

A second set of experiments were performed using fine grain solid particles rather than frozen liquids. The solids used all had long proton T_1 relaxation times when coarse grained and included sodium bicarbonate, potassium bicarbonate, barium chlorate monohydrate, maleic acid, borax and pyridone. In each progressive grinding to reduce the particle size lead to progressive shortening of the proton T_1 .

In the cases of maleic acid and barium chlorate monohydrate the ^2D NQR spectra were monitored as a function of grain size and as in the previous examples the NQR spectra were unaltered. Similar experiments were performed on the ^{14}N NQR spectrum of pyridone, again no change was observed in the NQR spectra of the fine powders.

The same experiments were performed on analar sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). As in the previous examples the proton T_1 was shorter for samples of smaller grain size. The NQR spectra of ^{23}Na corresponding to different grain sizes are shown in Fig. 1. All these spectra were obtained using a cycle time of 200 seconds with an irradiation time in zero applied field of 1.5 seconds and an irradiating magnetic field of amplitude 6 gauss peak to peak. All these spectra were obtained at 77K.

INSERT FIGURE 1

The spectrum shown in Fig. 1(a) is from a sample ground in a ball mill for 19 hours (sample A). It consists of four spectral lines at 720, 810, 980 and 1460 kHz. The sodium

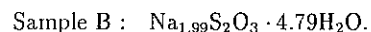
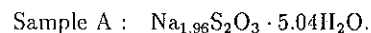
^{23}Na nucleus having a spin of $3/2$ has a NQR spectrum that consists of a single transition in zero applied magnetic field, therefore these transitions correspond to four inequivalent ^{23}Na sites within the crystal.

The spectrum in Fig. 1(b) is from a sample ground for 58 hours (sample B). In this case the spectrum consists of two transitions at 480 and 1325 kHz consistent with only two inequivalent sites in this sample. The third spectrum shown in Fig. 1(c) is from a sample of intermediate size between that of samples A and B. This sample (sample C) was produced by grinding a sample for 28 hours and then passing the fine powder through a sieve of mesh size of 105 microns. The spectrum for this sample contains all the spectral lines present in the spectra of samples A and B as expected for a sample of intermediate size.

Using an atomic absorption spectrometer the concentration of sodium ions in samples A and B were measured. The concentration of the $\text{S}_2\text{O}_3^{2-}$ ion in these samples was measured by titration and the results of these analyses are shown below.

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	Wt% Na	Wt% $\text{S}_2\text{O}_3^{2-}$	Wt% H_2O
Expected	18.5	45.2	36.3
Sample A	18.2	45.2	36.6
Sample B	18.8	45.9	35.3

therefore the compositions of samples A and B are given by



The deuterium spectra of samples A and B were compared using a deuterated sample and in this case no differences were observed between a sample ground for 12 hours and one ground for 58 hours. This is further evidence that the chemical state of this sample is

unaltered by the grinding procedure. The reason for the changes of quadrupole coupling constants of ^{23}Na with grinding in this sample is not known.

GENERAL CONCLUSIONS

From these experiments it can be concluded that the increase in the ratio of molecules on the surface to molecules in the bulk is responsible for the shortening of relaxation times.

It is known⁸ that the phonon spectrum is different on the surface than in the bulk and the oscillations of molecules on the surface have larger amplitude, especially normal to the surface. The higher mobility of the molecules on the surface is most probably responsible for the short relaxation times of the spins on the surface. This fact is best illustrated experimentally. When polylayers of material are adsorbed on the surface of different absorbents, the relaxation times of protons are normally several orders of magnitude shorter than those of the bulk.

However, the short relaxation times of the spins on the surface cannot be the only factor in reducing the relaxation times of the powdered samples since the molecules on the surface are only a few percent of the molecules in the bulk even for fine powders. For example, suppose the spins up to 4 nm away from the surface (approximately 15 layers) have very short relaxation times. The number of spins in this spherical shell would represent only 0.048% of the total spins in a grain 50 microns in diameter. Therefore, another mechanism should also participate in this process.

Bloembergen² suggested that the spin-spin diffusion process is responsible for transferring heat from the bulk to the spins near the paramagnetic impurities which in turn discharge the heat to the lattice through interaction with the impurities. In this case the same mechanism is responsible for transferring heat to the spins on the surface which, despite

their very low thermal capacity, are very effective. Since the spin-lattice relaxation time of the spins on the surface is very short they can easily discharge the heat received from the bulk to the lattice.

THEORY

A simple model for the process of spin-lattice relaxation in a powdered sample can be developed by assuming the following points:

- a) The spin-lattice relaxation time of spins on the surface of the grains is much shorter than that in the bulk.
- b) When a non-magnetized sample is placed in the magnetic field, due to the fast relaxation time of the spins on the surface these spins reach the lattice temperature faster than those in the bulk. Therefore, the spins in the bulk reach the thermal equilibrium through direct interaction with the lattice as well as through transfer of heat to the surface through the spin-spin interaction.
- c) To simplify the problem the grains of powder are assumed to be spherical and the diffusion to be radial.

Let $M(\underline{r}, t)$ represent the z -component of the magnetization per unit volume at position \underline{r} and time t . The rate of change of $M(\underline{r}, t)$ due to direct relaxation to the lattice in the bulk is

$$[\partial M(\underline{r}, t)/\partial t]_{\text{bulk}} = -[M(\underline{r}, t) - M_0]/T_1 \quad (1)$$

where M_0 is the equilibrium value of magnetization per unit volume at the lattice temperature in the applied magnetic field H_0 and T_1 is the spin-lattice relaxation time in the bulk.

The spin-spin diffusion process has been discussed by various authors^{1,2,9-12}. In this case it is responsible for transportation of heat from the bulk to the surface and can be written as

$$[\partial M(\underline{r}, t)/\partial t]_{\text{diffusion}} = D\nabla^2 M(\underline{r}, t) \quad (2)$$

where D is the diffusion coefficient and is given approximately by $D = a^2/50T_2$ for a simple cubic lattice. Here a is the lattice spacing and T_2 is the spin-spin relaxation time. The diffusion coefficient for non-conducting solids is typically of order 10^{-12} cm²/s.

The total time rate of change of $M(\underline{r}, t)$ can be written as

$$[\partial M(\underline{r}, t)/\partial t]_{\text{total}} = [\partial M(\underline{r}, t)/\partial t]_{\text{bulk}} + [\partial M(\underline{r}, t)/\partial t]_{\text{diffusion}} \quad (3)$$

By substituting equations 1 and 2 into equation 3 and assuming $m(\underline{r}, t) = M(\underline{r}, t) - M_0$ we have

$$[\partial m(\underline{r}, t)/\partial t] = D\nabla^2 m(\underline{r}, t) - m(\underline{r}, t)/T_1 \quad (4)$$

Taking into account the spherical symmetry of the problem, equation 4 can be written as

$$\partial[rm(r, t)]/\partial t = D\partial^2[rm(r, t)]/\partial r^2 - [rm(r, t)]/T_1 \quad (5)$$

The boundary conditions can be fixed by assuming that the sample is initially non-magnetized and that the spins on the surface reach the full magnetization instantaneously.

Therefore

$$m(b, 0) = M(b, 0) - M_0 = 0$$

$$m(r, 0) = M(r, 0) - M_0 = -M_0$$

Using the above boundary conditions in equation 5, the magnetization over the volume of a grain with radius b ($m_v(t) = 4\pi \int_0^b m(r, t) r^2 dr$) can be written as:

INSERT FIGURE 2

$$M(t) = M_{0v} \left\{ 1 - e^{-\left(\frac{t}{T_1} + 1\right)} \left[1 + (6/\pi^2)(e - 1) \times \sum_{n=1}^{\infty} (1/n^2) e^{-(\pi^2 \pi^2 D t / b^2)} \right] \right\} \quad (6)$$

where $M_{0v} = M_0(4\pi b^3/3)$.

DISCUSSION

In order to compare equation 6 with the experimental results several limitations of the model should be pointed out.

- a) The samples were ground with a ball-mill so the grains of the powder are neither spherical nor uniform in size. For example, maleic acid was ground for 10 hours and the size of the particles was measured using an electron microscope. This revealed a distribution of particles ranging from 5 microns to 40 microns in radius, with an average radius of 10 microns. The radii quoted represent the radii of the circles with the same area as the grains. Therefore, the assumption of spheres of equal volume is, of course, artificial.
- b) In developing the theory it was assumed that only the surface of the sphere is maintained at a fixed temperature. However, in the case of the powdered samples, the spins in several outer layers of each grain have very short relaxation times⁸. So the actual diameters of the grains will be larger than the calculate one and the magnetization of the spins in the outer layers will contribute as a base line to the magnetization curve.
- c) Finally the grains posses dislocations which correspond to extra surface area, making the calculated diameter even smaller than the real average diameter of the grains.

With all the above considerations it is clear that the theory presented is an order of magnitude calculation and the general shape of the magnetization curve is the best test for the theory rather than the values of the parameters derived from it.

In Fig. 2 the experimental points for maleic acid (ooo) with different sizes of particles are fitted to equation 6 with $T_{1s} = 0$. Due to the coefficient $(1/n^2)$ of each exponential in the sum, only the few initial terms in the summation are effective. In these fits the summation is extended up to $n = 5$. Fig. 3 represents the same functional fitting for borax in this case with n extended up to 10 because of the higher T_1 in this case.

The use of fine powders of solids or small particles of frozen liquids is a very good substitute for the method of inclusion of paramagnetic impurities in material in order to obtain short T_1 's. Of course this is only applicable when the use of single crystals is not required such as in NQR where only short range order needs to be maintained to observed the desired effect.

INSERT FIGURE 3

The use of the small particles method has several advantages over the inclusion of paramagnetic centres, such as:

- a) The inclusion of paramagnetic impurities in different materials is not always possible and is sometimes ineffective.
- b) The inclusion of paramagnetic impurities can change the structural form of the material in the area of observation.
- c) The inclusion of paramagnetic impurities destroys the sample purity, however with the grinding method if the reduction in T_1 causes a detrimental effect the original specimen may easily be reconstituted by recrystallization from solution.

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FIGURE CAPTIONS

Figure 1: The ^{23}Na NQR spectra from samples of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ of varying grain size. The top spectrum (a) is from sample ground in a ball mill for 19 hours, the middle spectrum (b) is from a sample ground for 58 hours and the lower spectrum (c) is for a sample with grain sizes between those of (a) and (b). All these spectra were obtained using a cycle time of 200 seconds with an irradiation time in zero applied magnetic field of 1.5 seconds and radio-frequency magnetic irradiation of amplitude 6 gauss peak to peak, the temperature in all cases was 77K."

Figure 2: The relaxation curves for maleic acid for various periods of grinding in a ball mill. In each case the experimental points (o o o o) are superimposed with a theoretical curve (solid line) generated using the function given in equation 6 with the best fit parameters stated with each curve.

Figure 3: The relaxation curves for Borax in an unground sample and a sample ground for 44 hours. In each case the experimental points (o o o o) are superimposed with a theoretical curve (solid line) generated using the function given in equation 6 with the best fit parameters stated with each curve.

TABLE CAPTION

Table 1: The approximate high and zero applied magnetic field proton spin lattice relaxation times (T_1 and T_{1D}) of a number of adsorbates on several adsorbents compared with typical values for the bulk samples.

TABLE 1

ADSORBATE	ADSORBENT	T_1 (s)	T_{1D} (s)	COMMENTS
Benzene	—	1614	< 1	Bulk sample
Benzene	γ -Al oxide	< 1		
Aniline	—	585	1	Fast cooling
Aniline	γ -Al oxide	14	< 1	
Aniline (degassed)	γ -Al oxide	3.9	< 1	
Aniline (oxidized)	γ -Al oxide	2.7	< 1	
Aniline	γ -Al oxide	3.8		Single layer + D2O
Aniline	vermiculite	10	< 1	
Aniline	mol. sieve 5A	4.8	< 1	
Aniline	silicate	4.5	1.4	
Phenol	—	300	2	Bulk sample
Phenol	γ -Al oxide	6.3		
Pyrrole	—	420		Bulk sample
Pyrrole	γ -Al oxide	11.6	3.2	
Benzamine	—	10		Bulk sample
Benzamine	γ -Al oxide	5.5		

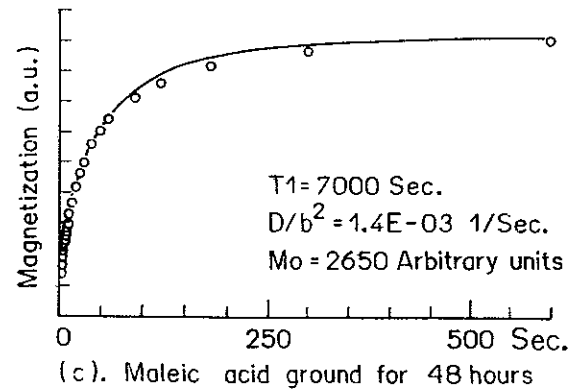
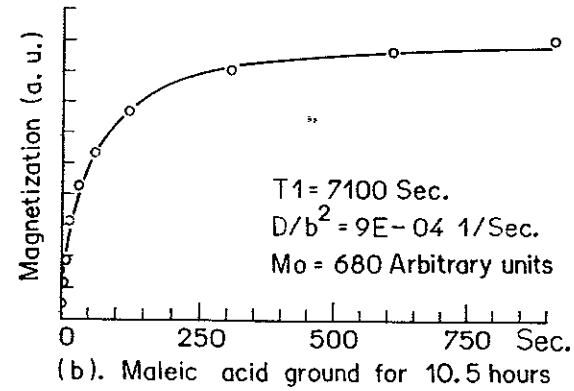
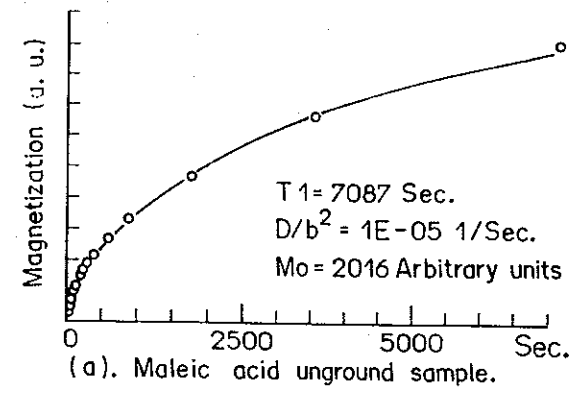
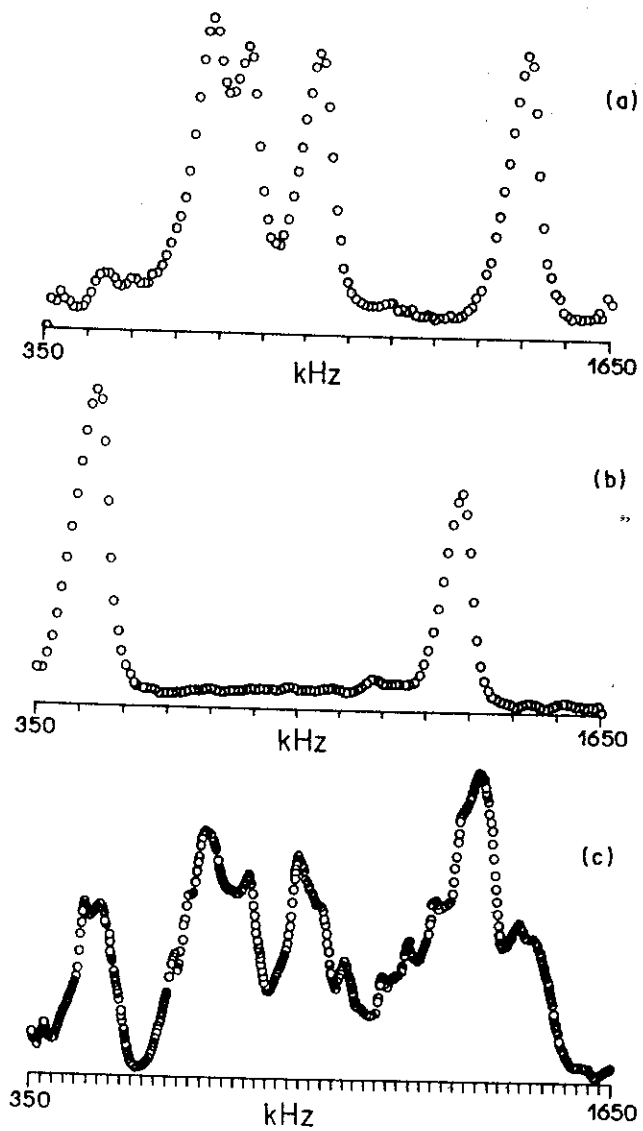
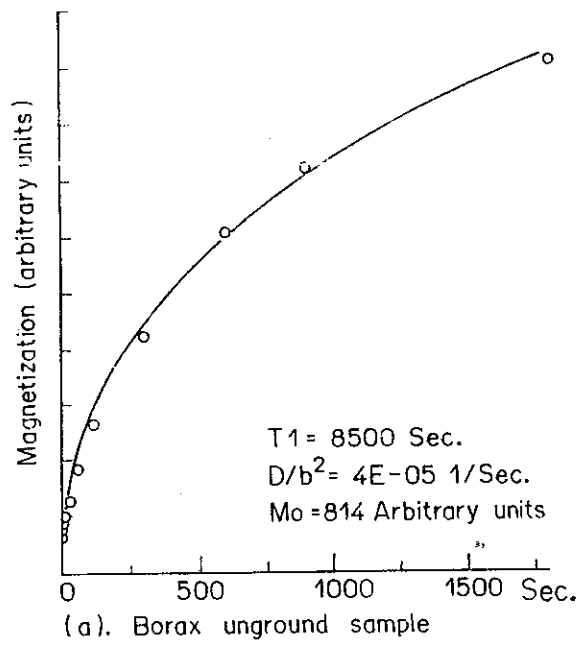
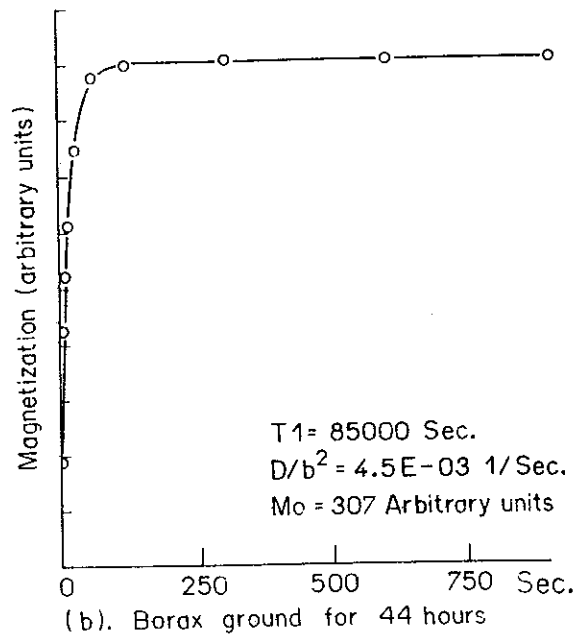


Fig.1
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Fig.2
 Said R. Rabbani et.al. "Nuclear Spin-Lattice Relaxation Reduction in ..."



(a). Borax unground sample



(b). Borax ground for 44 hours