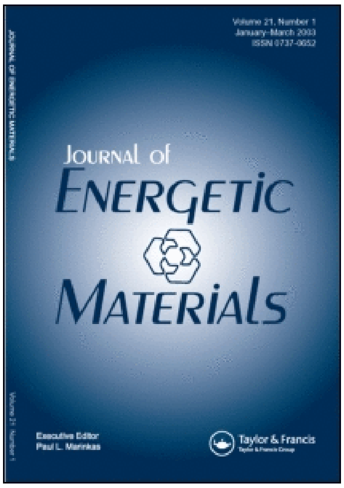

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INVESTIGATION OF PHASE TRANSITIONS IN AMMONIUM NITRATE BY NITROGEN-15 NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

Exploratory Nitrogen-15 nuclear magnetic resonance (NMR) studies of ammonium nitrate (AN) have been undertaken using both conventional and magic angle spinning (MAS) methods. The chemical shift anisotropy is measured by two different methods at room temperature, and a precise measurement of the difference in isotropic chemical shift occurring at the phase transition IV to III is reported. Finally, the activation energy for the motion of both ions in the room temperature phase are obtained. No evidence in discontinuity of nitrogen relaxation times across the phase boundary at 32°C was observed.

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INTRODUCTION

The many commercial and military uses of ammonium nitrate (AN) have resulted in considerable attention by researchers to the interesting crystallographic phase transformations of this substance. Two problems in its applications, namely hygroscopicity and dimensional instability, are closely related to some of its temperature dependent phase transformations. Our aim in this work is to determine the usefulness of nitrogen-15 nuclear magnetic resonance (NMR) and magic angle spinning (MAS) NMR in understanding the properties of this substance with respect to its phase transformations.

Below its melting point at 169°C, AN exists in a succession of solid phases[1,2] characterized by decreasing mobility of the ions. Transitions among these phases have been studied by several techniques in the past, including x-ray[3] and neutron diffractions[4] and Raman scattering.[5,6] In previous NMR studies[7] pertinent to this work, translational and rotational diffusion of the ammonium ion has been studied in some detail by proton and deuteron spin relaxation times (ref 7 and references therein). On the other hand, the nitrate ion has received much less attention, probably because of the complications presented by the quadrupolar interaction present in the abundant species of nitrogen and the poor natural abundance of Oxygen-17. With the advent of MAS-NMR techniques, however, Nitrogen-15 NMR studies in solids have become more possible, and together with the commerical availability of

^{15}N-enriched ammonium nitrate they provide us with the primary means to undertake this study.

Table 1 summarizes the well-known characteristics of the phase transitions of AN for convenience in the following discussions.

TABLE 1

Polymorphism of Ammonium Nitrate

Transition	Temperature, °C	Δ Volume, %
V → IV	-18	-0.9
IV → III	32.1	3.4
III → II	84.2	-1.6
II → I	125.2	+1.9
I → Liquid	169.6	-

V	- Tetragonal (α)	Brittle
IV	- Orthorhombic (β)	Brittle
III	- Orthorhombic (γ)	Brittle
II	- Tetragonal (δ)	Brittle
I	- Cubic (ε)	Plastic

EXPERIMENTAL

All the experimental data included in this report were obtained at the NMR facility at the U.S. Army Armament Research and Development Center (ARDC), which consists of a Varian Associates XL-200 NMR spectrometer with a super-conducting magnet. This instrument is equipped with a Nitrogen-15 solid sample probe with a MAS head and typical turbine speeds of 2200 Hz are obtained for packed polycrystalline samples. Pulse sequences to perform cross-polarization and high-power proton decoupling (100 watts) are available for use with this probe. Approximately 0.6 g of sample is packed into a Kel-F rotor for each series of experiments. In addition, a conventional broad-band probe for high resolution work is available which is capable of sample temperature variation and control in the range of -150° to 200°C. This probe uses standard 10 mm diameter glass tubes for samples filled typically, to 3 cm height.

RESULTS AND DISCUSSION

Room Temperature Studies

The Nitrogen-15 NMR spectrum of polycrystalline AN at room temperature is shown in Figure 1. It was obtained with the broad-band probe of the Varian XL-200 spectrometer in a sample with 99% Nitrogen-15 enrichment by signal averaging 10,000 scans. Two well-resolved but broad features were observed, corresponding to the two chemically distinct nitrogen sites in AN. The lines were considerably broadened by the dipole-dipole interaction with the protons in the sample and, in the case of the planar nitrate ion, by considerable chemical shift anisotropy.

Both of these sources of broadening could be drastically reduced by combining the techniques of MAS of sample and high power decoupling (HD). The resulting spectrum was shown in Figure 2. The drastic reduction in linewidth for each line is to be noted as well as the appearance of sidebands at reduced amplitude at multiples of the sample spinning frequency. A consequence of the reduction in linewidth is an enhancement of the peak signal to noise (s/n) ratio. Figure 2 was the result of a single NMR scan, compared to 10,000 for Figure 1. Examination of the spectra shown in the first two figures enables one to draw the following conclusions.

The isotropic chemical shift for the ammonium and nitrate ions in polycrystalline AN are not significantly different from those of the ions in solution. This result was not unexpected, but it implies that no particular insight about the structure of the solid is obtained from the isotropic chemical shift.

The anisotropy in the chemical shift of the nitrate ion obtained from Figure 1 is approximately 200 ppm. However, the $^{15}NO_3^-$ peak shows a shoulder on the down field side which indicates axial asymetry.

The variation in the amplitude of spinning sidebands as a function of the sample spinning speed in a MAS experiment can yield an independent value of the chemical shift anisotropy[8]. We undertook these measurements obtaining the spectra displayed in Figure 3. Analysis of these data yields the results:

$$\sigma_{33} - \sigma_{12} = 220 \pm 15 \text{ ppm}$$

$$\sigma_{11} + \sigma_{33} - 2\sigma_{22} = 120 \pm 40 \text{ ppm}$$

Finally, relaxation time measurements in AN were undertaken in preparation for temperature dependence work. T_1, the spin lattice relaxation time, was found to be in excess of 100 s for both sites in AN. Before such elevated values can be taken seriously, it is generally required that careful sample preparation procedures be undertaken to insure the absence of effects from paramagnetic species. In the absence of these precautions, we take 100 s as the lower limit for T_1. $T_{1\rho}$ the spin lattice relaxation time in the rotating frame, is sensitive to motions at much lower frequencies than T_1. The MAS solids probe allowed convenient measurement of this parameter with the following results:

$$^{15}NO_3^- \quad : \quad T_{1\rho} = 10.3 \text{ s}$$

$$^{15}NH_4^+ \quad : \quad T_{1\rho} = 19.2 \text{ s}$$

Temperature Dependence Results

Relaxation Time Measurements Near Room Temperature

A temperature dependence NMR study of hte multiple phases of AN, using the AN, using the two techniques exemplified in Figures 1 and 2, are subject to the following constraints. The available broadband accessory allows temperature variation and control up to 200°C. However, the poor s/n ratio means that each relaxation time measurement will take tens of hours of integration time. On the other hand, the available MAS probe, which produces single scan spectra with s/n close to 300, is a fixed temperature unit.

A partial solution to this problem was obtained by controlled heating or cooling of the MAS turbine air supply. To avoid possible damage to the MAS probe, this method was used to vary the temperature only within the temperature range from -18°C to 45°C. In this way, values of T_1 were obtained and plotted versus the reciprocal absolute temperature (Fig. 4). From the slope of this graph it was concluded that the activation energy for the process responsible for the relaxation is

$$E_a = 4.5 \pm 0.3 \text{ KCal Mole}^{-1}$$

It was noted that within the resolution of this experiment no discontinuity was observed in T_1 across the phase boundary at 32°C.

Phase III to Phase IV Transition

In the course of these relaxation time experiments, it was possible to observe simultaneously the high resolution MAS NMR spectrum of both phase IV and phase III material as they coexisted in the sample volume. These observations confirm the reports in the literature that the transition from the room temperature phase

(IV) to the high temperature phase (III) is analogous to a "melting" transition. In fact, as the temperature of our NMR sample was allowed to drift from about 40° to room temperature over a 2 hour period, it was observed that the spectrum of one phase gradually decreaed in amplitude as the spectrum of the other phase gradually increased. These results are shown in Figure 5. The thermal properties of AN have been well characterized by differential scanning calorimetry studies[1] and it is presumed on that basis that the observations shown in Figure 5 represent "freezing" of phase III into phase IV material. This effect was easily reproducible in either direction by heating or cooling. Of course, due to coarse temperature control, we could not confirm the lack of histerisis in the phase transition.

As a consequence of these observations, it was possible to measure the difference in the isotropic chemical shift in the solid phases III and IV to considerable precision. The results indicate upfield shifts of the following magnitude in going from III to IV:

$^{15}NO_3^-$: 50•4 HZ

$^{15}NH_4^+$: 30•4 HZ

BROADBAND NMR STUDIES

Encouraged by the NMR results in the vicinity of room temperature, it was decided to extend relaxation time measurements to the higher temperature phases. The slope of the $T_{1\rho}$ data versus reciprocal temperature obtained by MAS-NMR seemed to imply that it might be possible to observe a minimum in $T_1\rho$ at higher temperature. This observation would have been very interesting because it could yield the correlation time of the motions responsible for relaxation; however, such a minimum was not observed.

Because the MAS solids probe could not be modified to operate at tempertures much above room temperature, it was decided to use the Varian XL-200 broadband probe temperature controller, rated up to 200°C to continue the study. In the absence of the narrowing power of MAS with high-power decoupling, however, the NMR spectra were very broad, and their s/n ratios were poor. Each T_1 and $T_1\rho$ measurement required six to ten runs of 2 to 15 hours each for a given temperature point. This disadvantage was not present in the highest temperature solid phase (phase I), however, because it was a "plastic" phase. In this phase the ions are undergoing tumbling sufficiently fast so that the NMR spectrum is motionally narrowed, as in a liquid. The spectrum of AN in Phase I is shown in Figure 6.

The three spectra given in Figures 1, 2, and 6 together constitute an excellent example of the two methods for line narrowing: motional narrowing and high-power proton decoupling with magic-angle sample spinning.

CONCLUSIONS

All the relaxation time data obtained are plotted versus reciprocal temperature in Figure 4. These data are to be compared to the ^1H NMR relaxation times reported in ref. 7, and reproduced in Figure 7 for convenience. The following conclusions may be drawn:

The T_1 data were uniformly high for all phases measured, with the exception of the plastic phase I. As was remarked earlier, these values above 100 s were suspect. In phase I, however, the gentle temperature dependence was in the direction expected for the high temperature limit, $\omega_o\tau >> 1$, where ωo is the ^{15}N NMR frequency and τ is the correlation time for the motion. T_1 values for phases III, IV, and V were observed to be uniformly high as in phase II. Because these values did not reflect any relaxation process of interest to this study, precise values were not measured, nor were they plotted in Figure 4.

In order to exclude the possibility of cross-relaxation between the two chemically distinct nitrogen sites, $T_{1\rho}$ measurements were undertaken using singly labelled samples of AN. Measurements at several temperatures above the ambient yielded the same value of $T_{1\rho}$ in both singly labelled ($^{14}NH_4{}^{15}NO_3$) and doubly labelled ($^{15}NH_4{}^{15}NO_3$) AN.

The constancy of $T_{1\rho}$ values for the $^{15}NO_3^-$ as the temperature was varied, is in sharp constrast to the steep temperature dependence of the proton NMR work (figure 7) described in ref. 7. The proton work was performed at an NMR frequency close to 20 MHz, roughly the same frequency for the ^{15}N NMR of this work. The near equivalence of the NMR frequencies meant that the minimum in plots of relaxation time versus reciprocal temperature ought to occur at comparable temperatures, if the relaxation processes were the same. But, comparing figure 4 to figure 7, one must conclude that the relaxation process for proton NMR in the high temperature phases of AN, namely translational diffusion of the ammonium ion[7] was not effective in providing ^{15}N NMR relaxation of either ammonium or nitrate sites.

Clearly, a proper ^{15}N NMR study of the phase transition of AN would require a variable temperature NMR solid probe. Falling back on broadband NMR techniques, as was done here, meant that the results were somewhat less conclusive.

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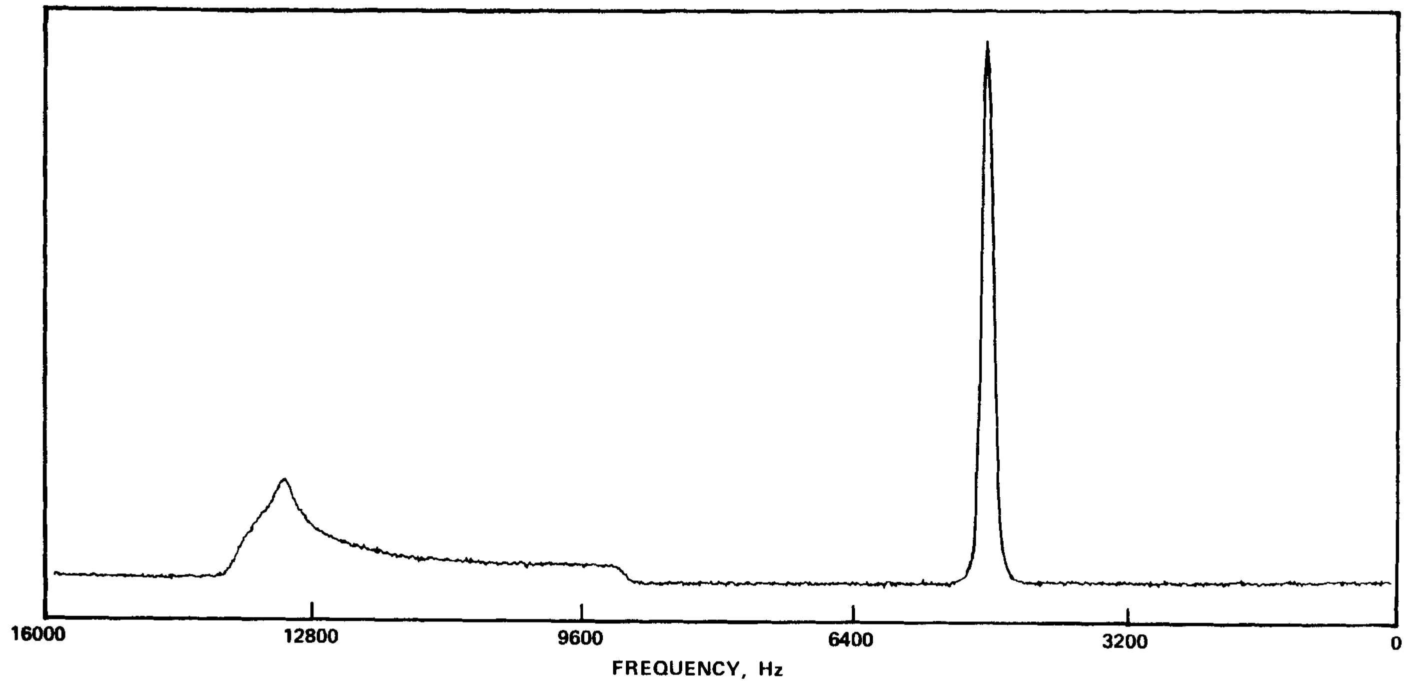

FIGURE 1
Nitrogen-15 NMR spectrum of double ^{15}N-labeled AN at room temperature obtained with the broadband probe

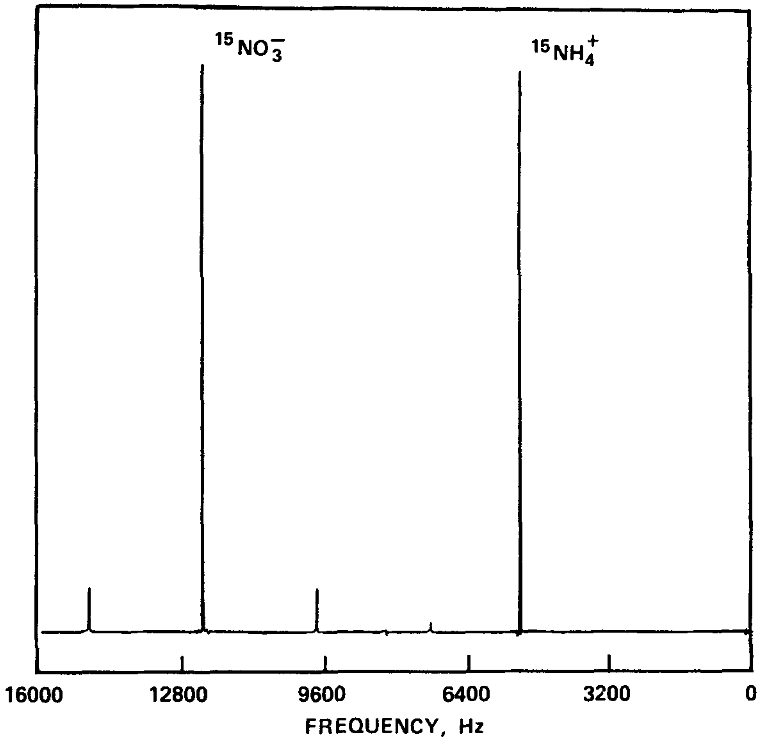

FIGURE 2
MAS Nitrogen-15 NMR spectrum of ^{15}N-labeled AN at room temperature obtained with the solids probe using CP and HPD

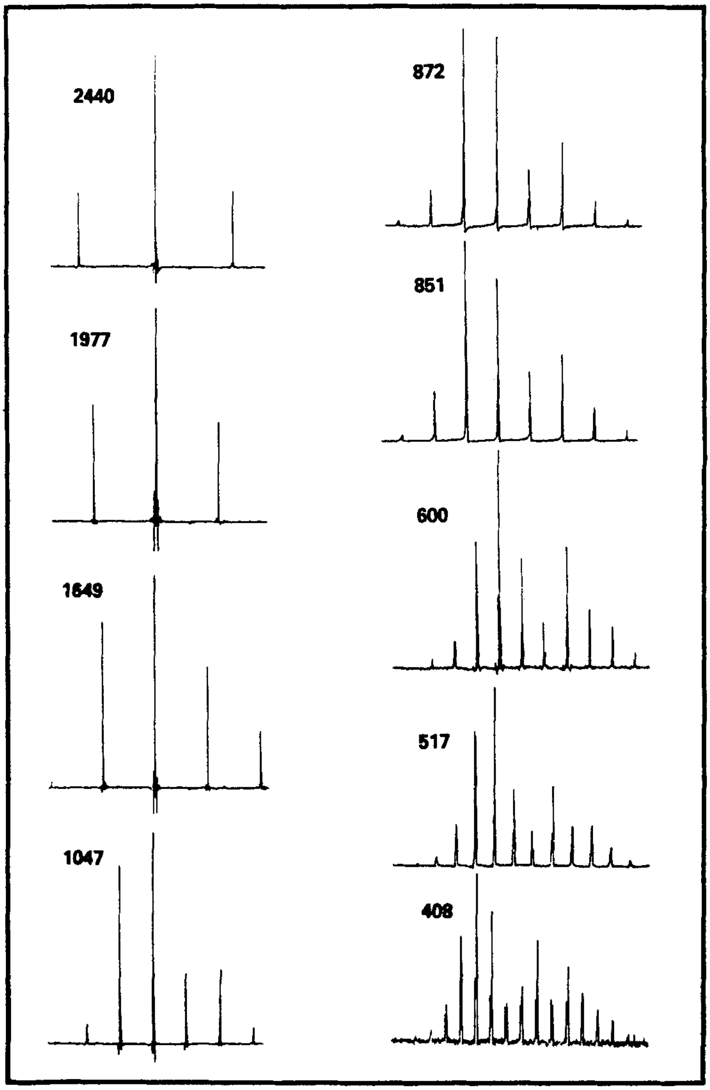

FIGURE 3
MAS Nitrogen-15 NMR spectrum of double ^{15}N-labeled AN for various spinning speeds (Hz, numbers in the figure)

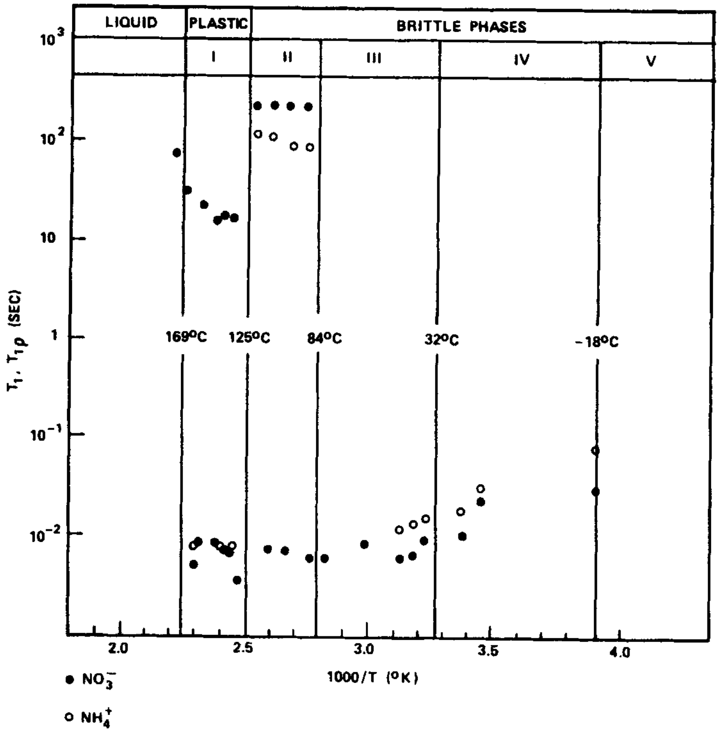

FIGURE 4

Nitrogen-15 NMR relaxation times T_1 and $T_{1\rho}$ for the nitrate and ammonium sites of AN versus reciprocal temperature

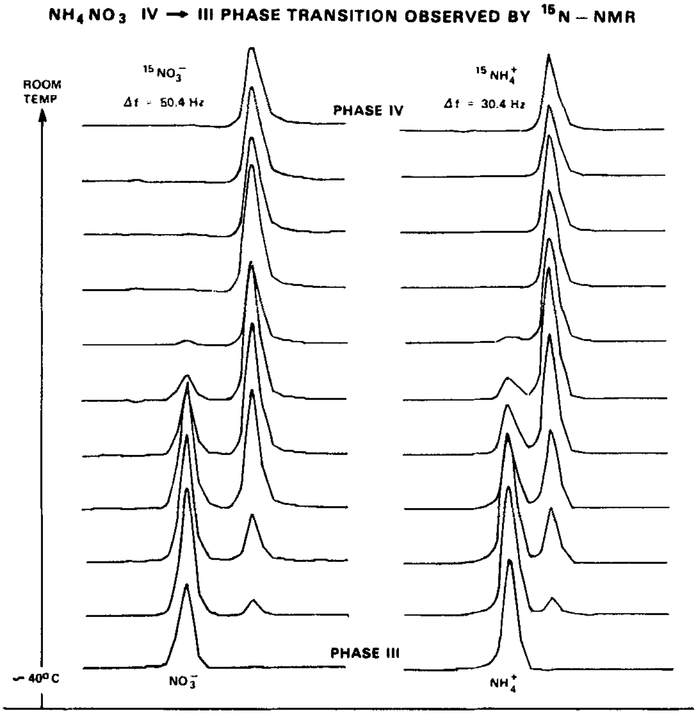

FIGURE 5
Observations of the "melting" phase transition in AN (III → IV) by CP/MAS/HPD NMR

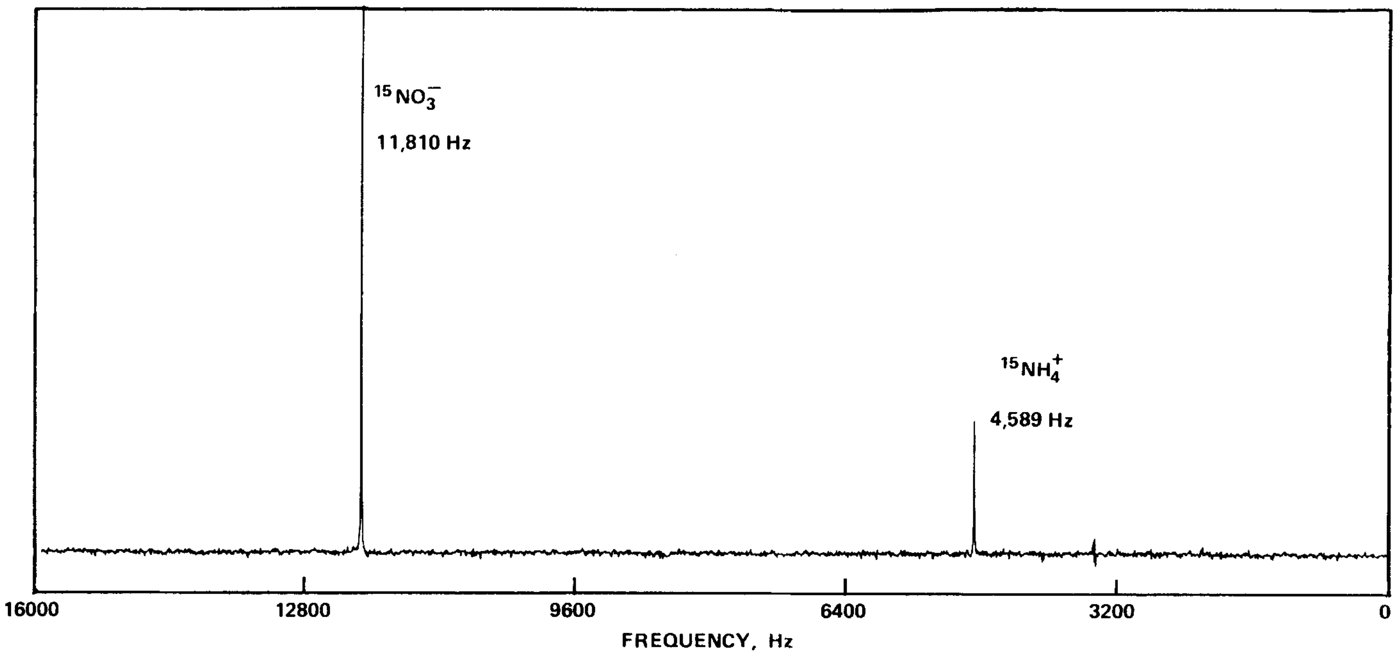

FIGURE 6
Nitrogen-15 NMR spectrum of double ^{15}N-labeled AN in its plastic phase (I) obtained with the broadband probe

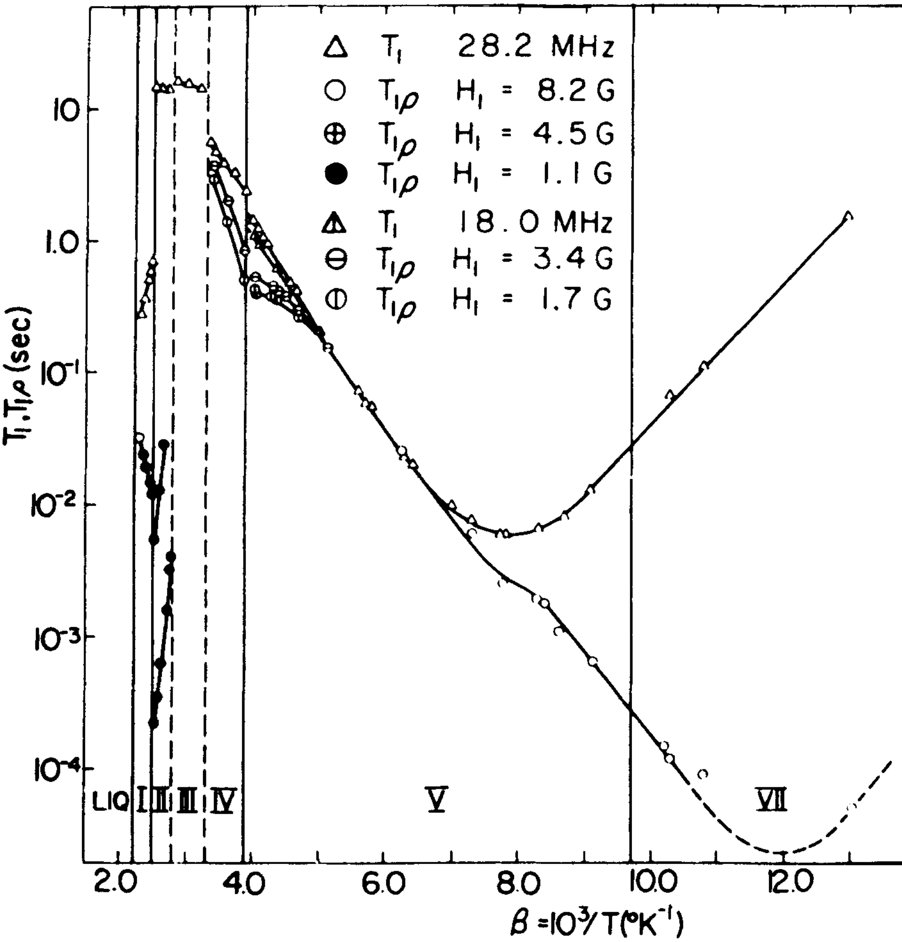

FIGURE 7
Temperature dependence of proton T_1 and $T_{1\rho}$ in polycrystalline NH_4NO_3 (reproduced from ref. 7)