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CARBON-13 NMR SPECTRA AND SPIN ECHOES IN SOLIDS[*†]

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Introduction

Recent developments have made carbon-13 nmr in solids an attractive spectroscopic tool.[1] It is not possible to cover everything in the limited format of this talk, so I shall limit the presentation to a brief description of a few aspects of the research. This should give some indication of the problems encountered and the information extracted. The presentation will include discussions of instrumentation, experimental details, high resolution spectra in crystals, chemical shielding tensors and spin echoes.

Double Resonance Spectrometer and Experimental Details

A wideband nuclear magnetic double resonance spectrometer has been constructed to permit the implementation of novel techniques for high sensitivity detection of nuclei of low isotopic abundance.[2] This spectrometer was used for the experiments to be described, the main application being the detection of ^{13}C in natural isotopic abundance in solids. For this purpose it is of high sensitivity and large signals are observed from small crystalline samples. The device has a fast programmable pulse unit which controls the radiofrequency modulation. This is interfaced to an on-line computer making the interchange of modulation sequences and the trial and implementation of new experiments extremely flexible. The computer also serves for on-line data acquisition, data analysis and filing.

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[†] To be presented at the Fifteenth Experimental NMR Conference, Raleigh, N. C., April 1974.

The magnet is a wide bore superconducting solenoid. Radiofrequency amplifiers are modified radio amateur transmitters operating at 26.7 and 106.2 MHz and capable of the large power output required for the solid state studies. The low level radiofrequency sections contain four phase channels for each frequency and operate in heterodyne mode with an intermediate frequency of 30 MHz.

An important component of the spectrometer is the sample probe. This is designed for the geometry of the superconducting solenoid and is equipped with homebuilt variable capacitors to withstand the large radiofrequency voltages across the sample coils. A crystal goniometer controllable remotely permits precise orientation and rotation of single crystals in the magnetic field. The crystal holder is designed to transfer directly to an X-ray goniometer allowing precise orientation of the crystals by X-ray precession methods. A picture of part of one probe which we have used is shown in Fig. 1.

High sensitivity and high resolution ^{13}C nmr spectra are provided by proton-enhanced nuclear induction spectroscopy[1] in which nuclear magnetic polarization is transferred from abundant ^{1}H to the rare ^{13}C nuclei. High power spin decoupling subsequently produces the requisite enhancement of resolution. The cross-polarization process can be repeated many times and the signals from the rare nuclei accumulated to yield a markedly enhanced sensitivity over conventional detection techniques. Figure 2 demonstrates the sensitivity enhancement with our spectrometer on a small polycrystalline sample of adamantane, depicting visually the accumulative cross-polarization process. In other cases, we have found it more convenient to effect a single shot cross-polarization from the proton system after adiabatic demagnetization in the rotating frame. Details of this as well as additional details of equipment and experimental procedure will be described in the presentation.

Carbon-13 Spectra, Chemical Shielding Tensors and Spin Echoes

Most investigations of magnetic shielding have been performed in isotropic liquid solution. Since, under these conditions molecules are reorienting rapidly, only one parameter, the isotropic shielding σ:

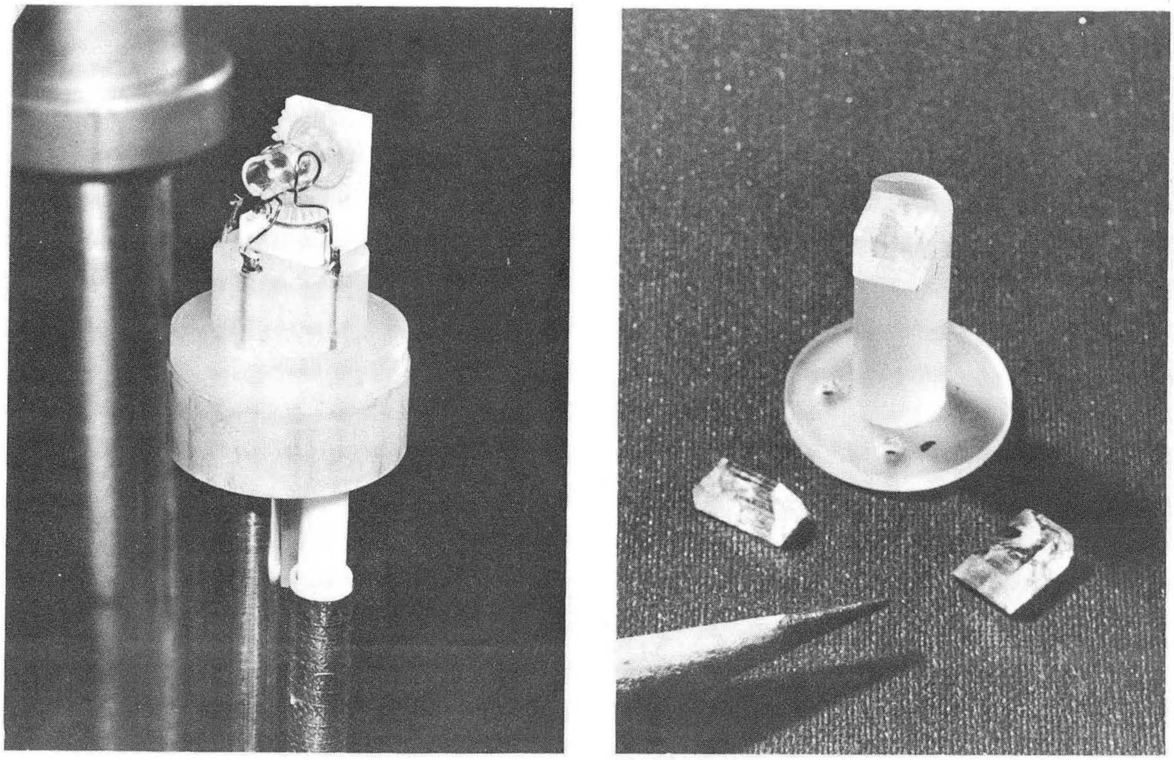

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Fig. 1. Double-resonance probe head and crystal holder for X-ray goniometer. The crystals are mounted in the Kel-F cube on the end of the holder; this keys onto the gear, allowing the crystal to be rotated inside the sample coils. The lower part of the probe contains the high-power tuning and matching electronics.

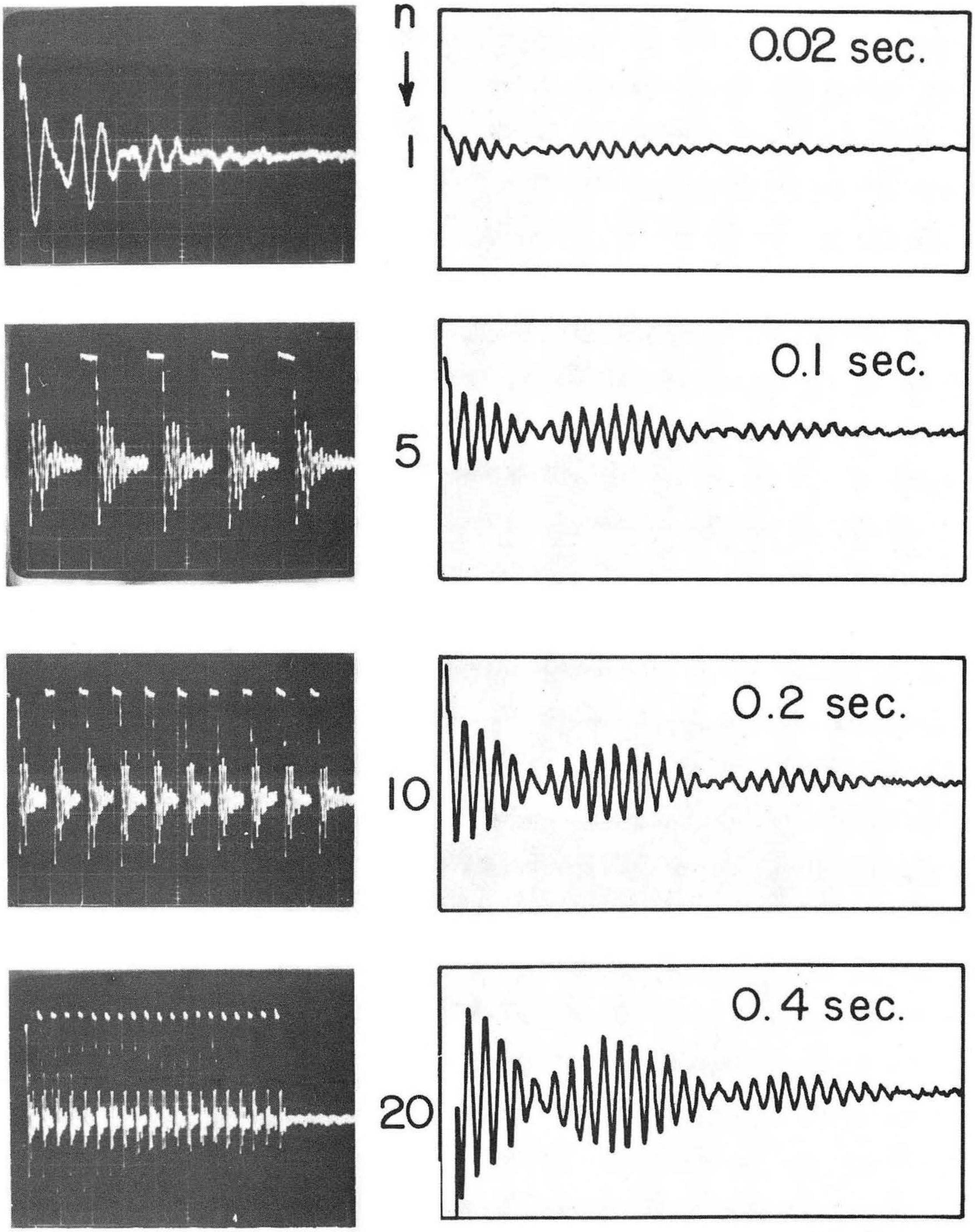

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Fig. 2. Demonstration of sensitivity enhancement for rare nuclear spins. The oscilloscope photographs on the left depict the output of the ^{13}C phase detector for various numbers (n) of $^{1}H \rightarrow ^{13}C$ cross-polarization steps in solid adamantane. The positive pulses are from rf receiver blocking during the cross-polarization, and they are followed by proton-decoupled ^{13}C-free precession signals. It is these which are rapidly transferred and accumulated by the computer. The cross-polarization pulses are 5 msec long. The traces on the right show the accumulated signals and acquisition times corresponding to the number of cross-polarizations one the left. These were recorded further off resonance for display purposes.

$$\sigma = 1/3 \text{ Tr } \boldsymbol{\sigma}$$

is extracted from such experiments. Full shielding tensors are available from single crystal studies employing the approach described previously, and I shall present recent results for carbon-oxygen groups in some organic single crystals.

Figure 3 shows part of the two molecules in the unit cell of ammonium d-tartrate ($NH_4^{+-}OOC\text{-}CHOH\text{-}CHOH\text{-}COH^{-+}NH_4$). In isotropic liquid with conventional nuclear magnetic resonance, only two lines are observed in the ^{13}C nmr spectrum since there are clearly only two magnetically inequivalent sites (CHOH and COO^-) over the isotropic averaging caused by molecular reorientation. In the crystal, using proton-enhanced nmr, we can distinguish light lines in some orientations from the eight carbon nuclei in the unit cell, as shown in Fig. 4. The crystal can be precisely oriented and rotated and analysis of the spectra for three sets of rotations yields the ^{13}C chemical shielding tensor.

Of particular interest is the orientation of the principal axes of $\boldsymbol{\sigma}$ in the molecules. This cannot be assigned unambiguously since an experiment determines σ only relative to the crystallographic axes. However, based on a number of experiments and assumptions which will be described in the presentation, a reasonable assignment can be made. This puts the most heavily shielded elements σ_{33} for the carboxy ^{13}C perpendicular to the COO^- plane and for the hydroxyl ^{13}C along the C-OH bond. The magnitudes of the principal elements and the orientation of σ will be described for a number of systems containing carbon-oxygen functional groups for which experiments have been completed.[3] In particular, mention will be made of the effect of hydrogen-bonding on the tensors.

We recently reported the observation of enhanced long lived ^{13}C nuclear spin echoes in solids.[4] If time permits, a discussion of how this is used to determine limiting attainable resolution for solid state ^{13}C nmr and to measure anisotropic diffusion will be presented. Details of the experimental procedures will be given and illustrated with some recent results. An example of the type of spin echoes observed is depicted in Fig. 5.

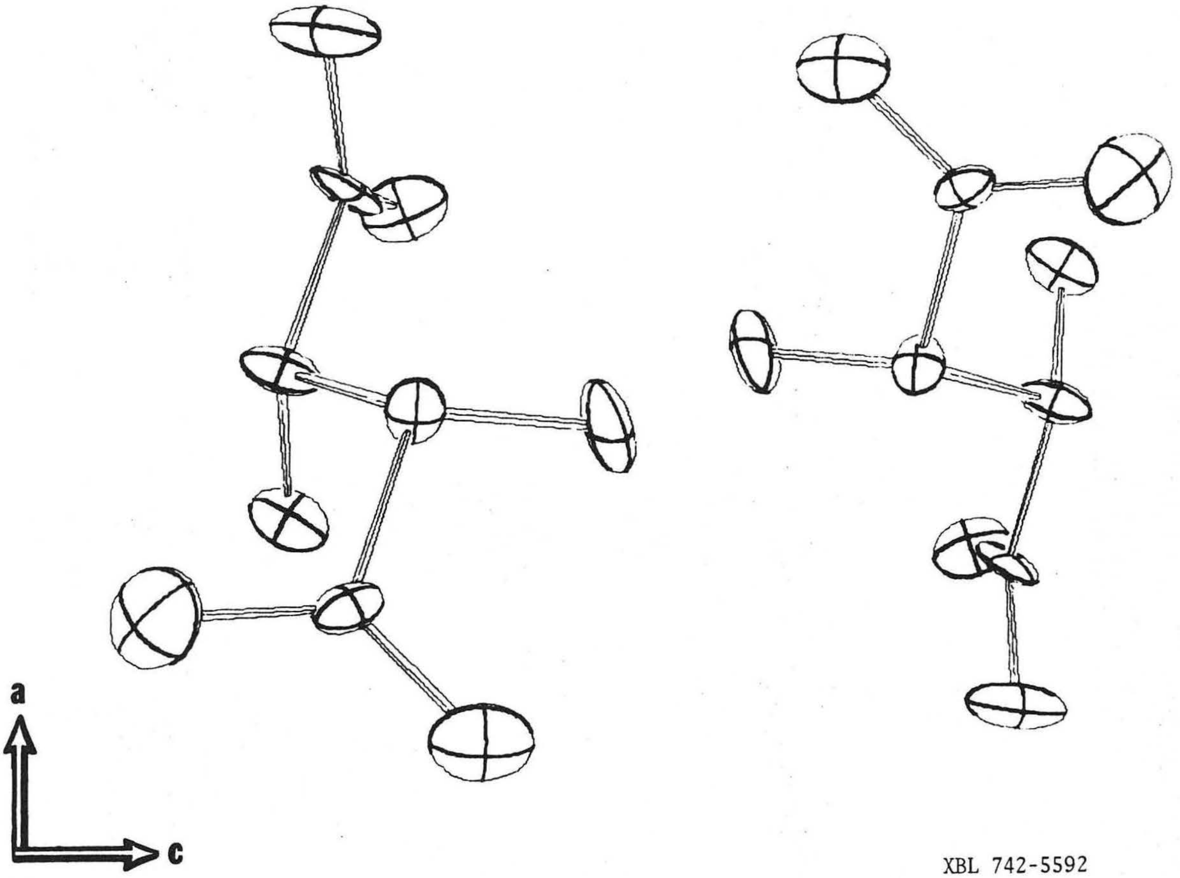

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Fig. 3. Perspective view along the crystallographic b axis of two tartrate ions (OOC-CHOH-CHOH-COO) showing the carbon and oxygen atoms in the unit cell of (D)-ammonium tartrate. In general orientations, the carbon nuclei will be in magnetically inequivalent positions.

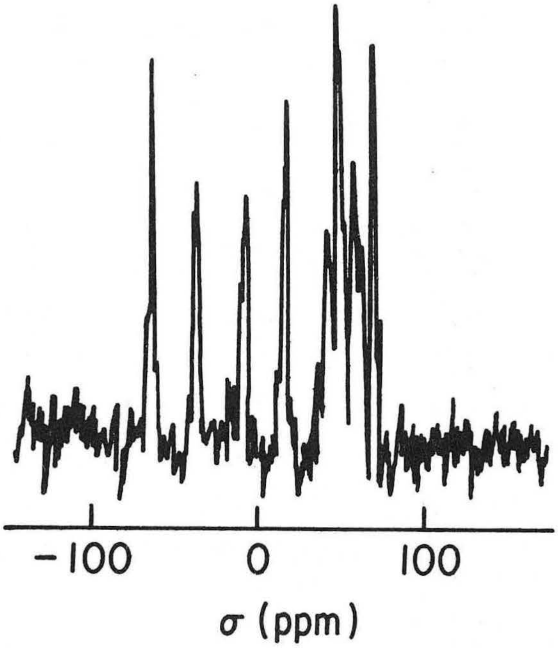

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Fig. 4. Fourier transfor ^{13}C nmr spectrum of single crystal (D)-ammonium tartrate (see Fig. 3), showing separate lines for each of the carbon nuclei. The high field lines are from the hydroxyl carbons and the low field lines from the carboxyl carbons. The horizontal axis is in ppm relative to an external reference of liquid benzene. In isotropic solution only two lines are observed.

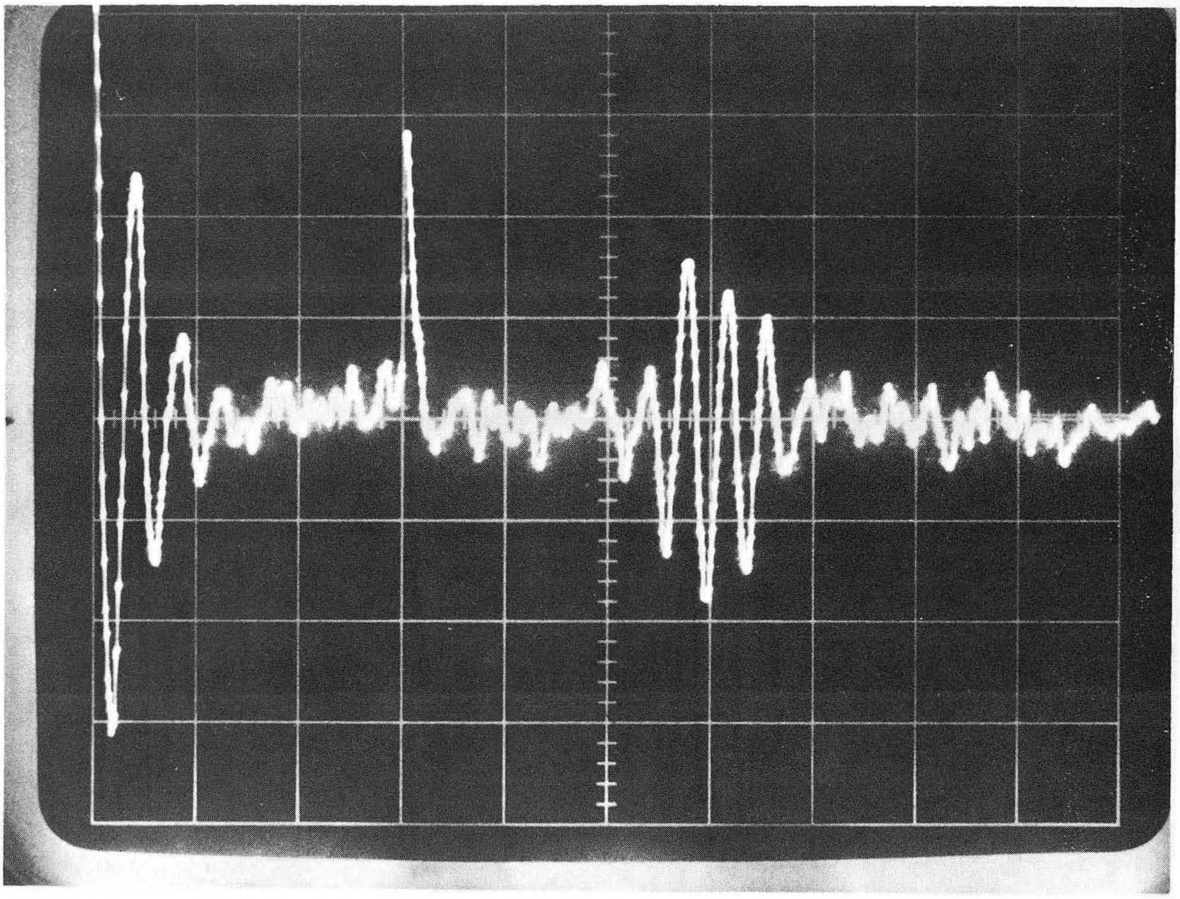

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Fig. 5. ^{13}C nuclear spin echo in solid adamantane. The sensitivity is enhanced by cross-polarizing the ^{13}C nuclei from the ^{1}H spin reservoir after adiabatic demagnetization in the rotating frame. Following the cross-polarization, a decay is observed in the magnetic field gradient. After a refocusing pulse at τ = 3 msec an echo is observed at 2τ = 6 msec during strong proton irradiation. From the decay of this echo amplitude vs τ, diffusion effects can be seen directly for the first time in solids and partially ordered systems. The oscilloscope scale is 1 msec/division.

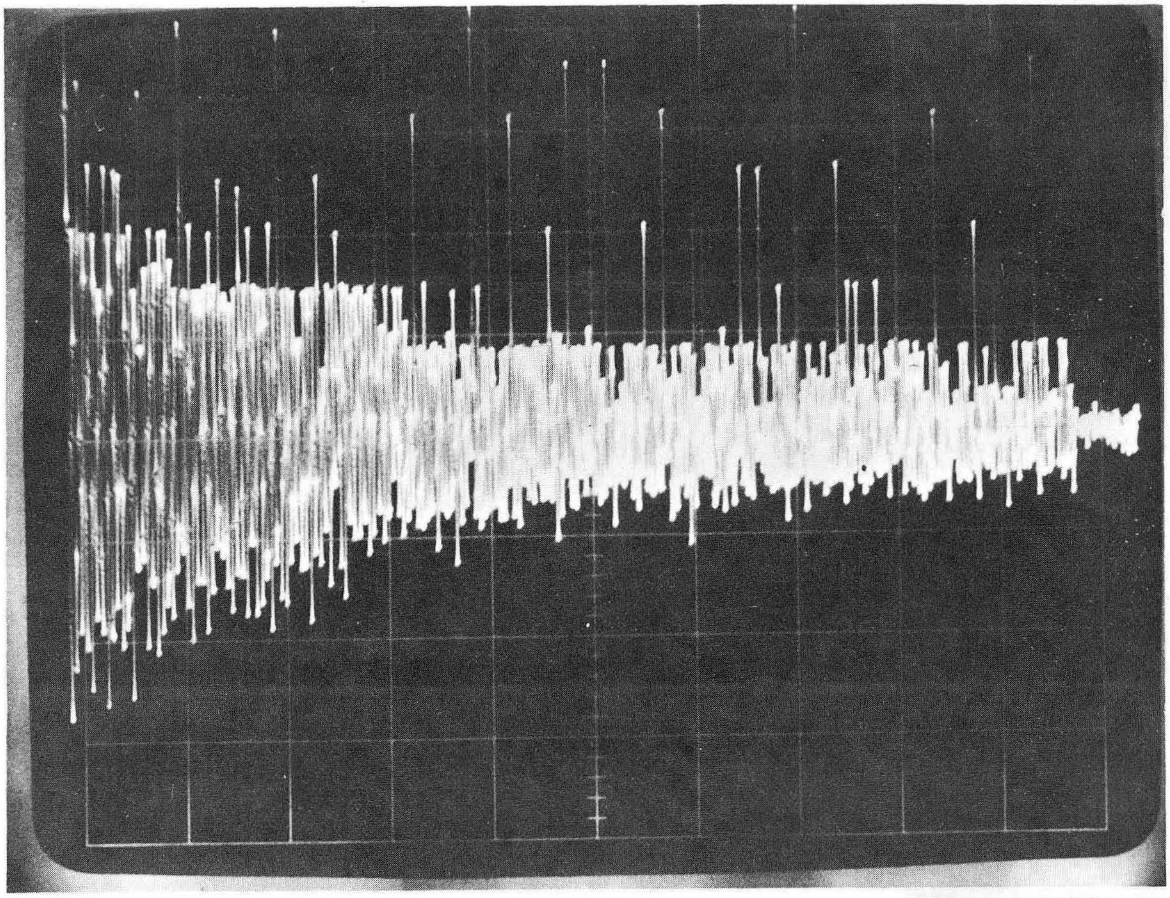

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Fig. 5 continued. Train of ^{13}C nuclear spin echoes in solid adamantane with enhancement and proton irradiation. This type of experiment allows the determination of the natural ^{13}C linewidth due to residual ^{13}C-^{13}C dipolar coupling and places a limit on the resolution attainable by this technique. In addition, the exponential envelope decay verifies the contention of Kittel and Abraham that as we go from periodic to random disposition of magnetic nuclei the line shape should change from Gaussian-like to Lorentzian-like to character. The oscilloscope scale is 10 msec/div.

The work described in this presentation was performed with J. J. Chang, T. W. Shattuck and the late E. Abramson, and in collaboration with R. G. Griffin visiting from the National Magnet Laboratory in Cambridge, Massachusetts. I am particularly grateful to D. D. Williamson for extensive assistance with the design and construction of equipment.

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