

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-08-0028

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1. REPORT DATE (DD-MM-YYYY) 11/30/2007		2. REPORT TYPE Final		3. DATES COVERED (From - To) 2/1/2007--- 11/30/2007	
4. TITLE AND SUBTITLE Solid-State Nuclear Magnetic Resonance Investigations of Microwave Tube Cathode Structure				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA 9550-07-1-0106	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) K. A. Smith				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Mexico Office of Research Administration Scholes Hall, Room 102 Albuquerque, NM 87131-0001				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR 875 N. Randolph St. Suite 324 Room 3112 Arlington, VA 22203-1768				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/PKR1	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT <i>Distribution Statement A: unlimited</i>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The objective of this work was to determine if Solid-State Nuclear Magnetic Resonance (NMR) would be able to determine what chemical or structural changes occur during treatment of carbon fibers by CsI, and during operation of treated cathodes. It was known that CsI treated carbon fibers are superior to either solid CsI or untreated fibers when used as cathodes for high power microwave production. For C-13 NMR, probe background was a major problem. Even after efforts to remove it, the signals were very broad. There was useful difference between samples. I-127 spectra were obtained from standards and treated cathodes. The iodine that is seen appears to be CsI. However, it is possible that not all the iodine is being observed. Cs-133 is less sensitive than either carbon-13 or iodine-127, and no signals were seen from samples. Electron spin resonance (ESR) was also run, and there is some indication of radical formation during cathode use. Based on these results, it does not appear that Solid-State NMR is a useful tool in investigating these systems.					
15. SUBJECT TERMS Solid-State Nuclear Magnetic Resonance					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON Karen Ann Smith
a. REPORT none	b. ABSTRACT none	c. THIS PAGE none			19b. TELEPHONE NUMBER (include area code) 505-277-4031

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

20080118120

Samples:

Only a small amounts of actual samples were available, therefore powdered graphite was used to set up carbon experiments. Solid and solution CsI, CsCl, and KI were used to set up cesium and iodine experiments.

Experiments were performed on five samples. Fibers from cathode CCVCA (55SB1-Z-C3-H2) with 1M shots on RTP 165kV will be referred to as "fiber 1". This sample was coated with CsI and shot. "Fiber 2" was CCVCA KB1 Cc C6 IS8. Both coated and uncoated fibers were available. This was not shot. The final source was a test cathode that was shot as a test dummy, but may or may not have been coated. Some of the fibers were plucked, and some were scraped off; they are referred to as plucked or scraped cathode.

ESR results:

The samples were studied with ESR (electron spin resonance) spectroscopy, which detects the presence of radical species and unpaired electrons. In the fiber 1 sample, a low intensity ESR feature was detected at a g factor of 2. This feature can be attributed to a radical species that is present in low concentration, presumably formed as the sample was shot. Other fiber samples did not display this ESR feature. Fiber 1 detuned the ESR probe, but the other samples did not. Detuning is indicative of a "lossy" sample, which can be due to radicals, or other electronic effects such as conduction. Even though the test cathode was also shot, there may be far fewer radicals present, especially if it was shot fewer times.

Carbon-13 results:

Initial experiments included Bloch decay, Bloch decay with proton decoupling, and Cross-Polarization (CP). All experiments were performed using Magic Angle Sample Spinning (MASS) at a spinning speed of 3 kHz. The spectra were very broad. There was no difference between the spectra with and without proton decoupling. This indicated that, as expected, there were few, if any protons in the sample. The lack of signal from the CP experiment confirmed the lack of protons. All further experiments were performed only as MASS with Bloch decay with no proton decoupling. Several relaxation times were tried, and there was no observed difference between a 10s delay and a 100ms one. Short relaxation times are consistent with the presence of radicals, but somewhat surprising in the unshot samples.

Probe background was a big problem. Background is from the probe, not the rotor or cap. As the sample signals are quite broad, they do not stand out from the background. Background suppression programs don't seem to help (both signal and background are diminished). Echo experiments eliminate both graphite and background. Subtracting the background is somewhat problematic as signals are broad. Background spectra were obtained under identical conditions to sample spectra. When these were subtracted, the result appears to be genuine peaks.

Filling the rotor with shot cathode dramatically detuned the probe. It was possible to retune- but the shift indicates a very lossy sample. Fiber 1 did not fill the rotor, it was placed in the center, and sandwiched between layers of salt (NaCl). It did not detune the probe- probably there was not enough to do so. Fiber 2 uncoated was run in a smaller rotor, it did not fill the rotor and did not detune the probe.

The graphite and cathode spectra after subtraction have a broad peak centered about 120 ppm. Fiber 1 and the background have no peaks after subtraction. Fiber 2 uncoated had a broad hump not much different from the background. Fiber 1 may have no observable peaks because radical formation may have broadened them out, or because there was not enough sample. Figure 1 contains some representative carbon spectra.

Iodine-127 results:

No proton decoupling or cross-polarization experiments were performed, as no protons were expected to be present near the iodine atoms. All experiments were performed using Magic Angle Sample Spinning (MASS) at a spinning speed of 3 kHz. Several relaxation times were tried, and there was no observed difference between a 10s delay and a 100ms one. Short relaxation times are consistent with a quadrupolar nucleus, regardless of the presence of radicals.

There was no probe background signals. There is a noise spike at about 300 ppm that appears in several of the spectra. Solid CsI has spinning sidebands that extend across the entire spectrum. This is expected for the quadrupolar iodine nucleus in a symmetric environment. No signals were seen from the plucked or scraped cathode samples, which may not have been treated with CsI, or from uncoated fiber 2. But, fiber 1 and coated fiber 2 samples have signals that match CsI in chemical shift and linewidth. The signal/noise is too low to see

the spinning sidebands. The iodine-127 that is observed appears to be identical to solid CsI. It is possible that not all the iodine is being observed. Quadrupolar nuclei in a very non-symmetric environment can broaden out so as to be unobservable. Figure 2 contains some representative iodine spectra.

Cesium-133 results:

No proton decoupling or cross-polarization experiments were performed, as no protons were expected to be present near the cesium atoms. All experiments were performed using Magic Angle Sample Spinning (MASS) at a spinning speed of 3 kHz. Several relaxation times were tried, and there was no observed difference between a 10s delay and a 100ms one. Short relaxation times are consistent with a quadrupolar nucleus, regardless of the presence of radicals. Cesium-133 is much less sensitive than carbon or iodine. While solid and solution CsI can be easily seen, no signal was seen from any of the cathode samples. The CsI is only on the surface, it is thought, which limits how much is present. As mentioned in the carbon section, putting too much sample in the probe detuned the circuit. This limits the amount of sample that can be studied. Figure 3 contains some representative cesium data.

Conclusions:

Solid-state NMR does not appear to provide a great deal of information on this system. Carbon spectra are broad and featureless. Iodine spectra are identical to that of CsI, indicating that at least some of the iodine remains as CsI. Cesium spectra have not been observed from actual cathode samples. ESR indicates some radical formation in shot samples, which is to be expected. There are NMR probes available with a much reduced carbon background signal. Spectra taken with these probes would not require the background suppression, and therefore subtle differences between samples might be observed. Some researchers have reported good results with very fast spinning (20kHz) of paramagnetic materials. The very fast spinning might improve the spectra of cathode materials.

Figure 1:

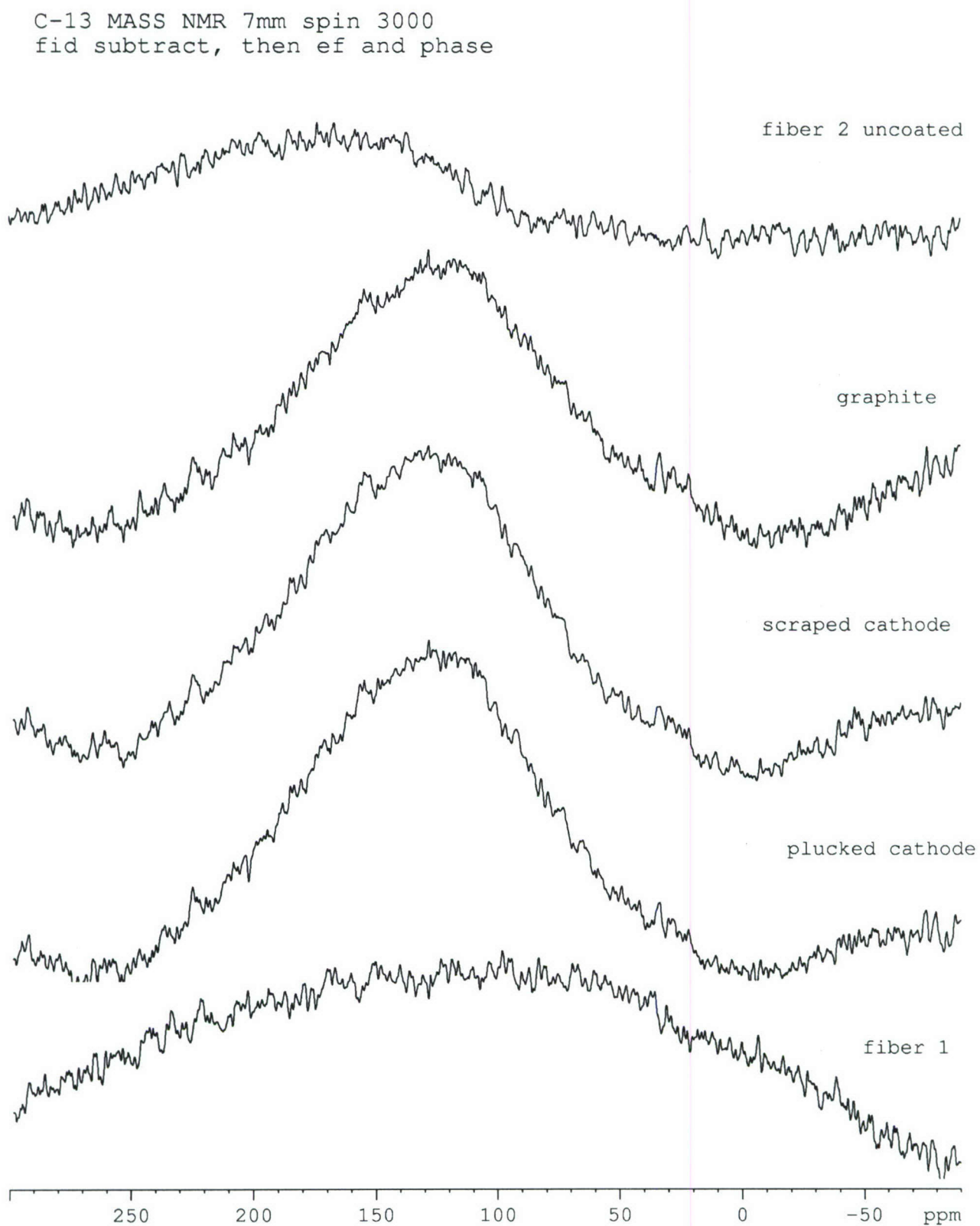


Figure 2:

Iodine-127 MASS NMR 7mm spin 3000

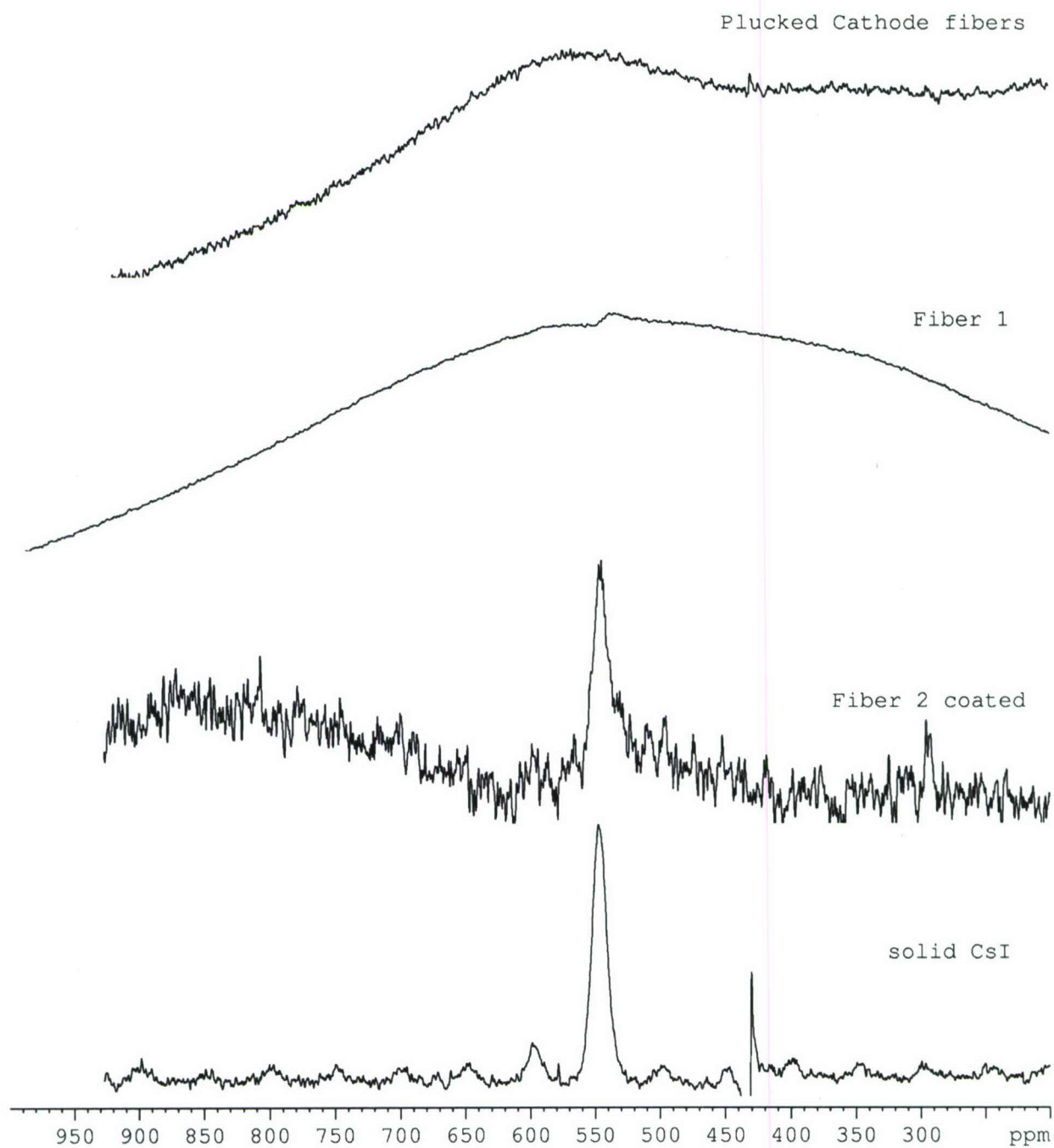


Figure 3:

Cesium-133 MASS NMR 7mm spin 3000

