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Acoustics in New Materials
Final Report October 1, 1999 - September 30, 2002

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N00014-01-1-0019
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This report summarizes the goals and accomplishments for ONR grant N00014-01-1-0019, "Acoustics in New Materials". The technical objectives of this research were to determine the physical properties of new materials with emphasis on thin films deposited on substrates. For the most part, experiments involved the measurement of elastic constants and damping. As derivatives of the free energy with respect to atomic positions, elastic constants are a sensitive probe of the environment in which all physical processes take place within a solid; they are a particularly important probe of phase transitions. For studies of thin films on substrates, these measurements yield information about how the film and substrate interact and modify behavior.

Published papers, invited presentations, personnel, etc.

Accomplishments during the three year period covered by this report include the publication of 11 refereed papers, 13 invited lectures, and the presentation of seven contributed papers at meetings. Of the 11 papers, one was an invited publication in the Reviews of Modern Physics, and two were published in the prestigious physics journals Physical Review Letters and Applied Physics Letters. Of the 13 invited lectures, three were university colloquia, two were lecture series at summer schools, and the rest were presentations at international meetings. Three patent disclosures were submitted.

Two graduate students received Ph.D. degrees, and one received a Master's degree; all continued working in acoustics in the US. Two post doctoral scholars were trained in this research program. A number of undergraduate students made significant contributions to the research.

A list of the publications, personnel, etc. is presented in the appendix. In the sections which follow, a summary of the research accomplishments is presented.

Technical Objectives

The technical objectives of this research are to use novel acoustic techniques to study the physics of new materials with emphasis on thin films deposited on substrates. The thin films to be measured initially include novel magnetic films and mats of carbon nanotubes[1-3],

which are the strongest fibers which can be made. The materials used for the magnetic films undergo a phase transition involving a state of colossal magnetoresistance (CMR)[4-7], and for CMR films, the interface with substrate has a strong influence on this transition[8-9]. The effects of a substrate interface on CMR and the mechanical properties of the carbon nanotube mats (as films of ~ 500 nm thickness on substrates) are both readily studied with a technique, small sample resonant ultrasound spectroscopy (RUS)[10-13], unique to this laboratory.

Technical Approach

Our approach for determining the elastic and damping properties of thin films involves small sample resonant ultrasound spectroscopy (RUS), a reliable and accurate technique which was developed in our ONR funded research. Ordinarily, RUS is used to determine the elastic properties of bulk samples; in this case, one measures the dimensions of a sample and a number of its natural frequencies of vibration, and from this information all of the elastic properties may be calculated. The natural frequencies are measured as shown in the figure; one transducer drives the sample at a corner, and at a diametrically opposite corner a second transducer monitors the response of the sample and detects resonances at the natural frequencies. Our laboratory is unique in its ability to measure very small samples, only a few hundred microns in dimension and less than 100 micrograms in mass. In order to measure the mechanical properties of a thin film, one measures the natural frequencies of a substrate on which a thin film is deposited, and (separately) the natural frequencies of the substrate alone. From the difference in the measured frequencies, all of the elastic and damping properties of the thin film may be determined. In order for a difference in the frequencies to be measurable, the substrate must not dominate the sample. Thus small substrates are necessary, and our unique small sample RUS technique is essential.

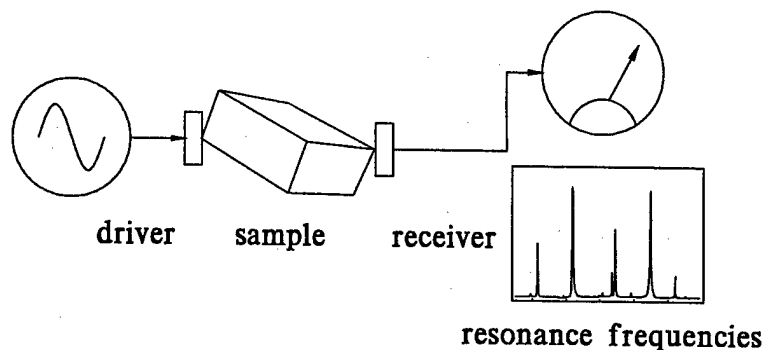


Fig. 1. Schematic of the Resonant Ultrasound Spectroscopy method.

Results

Results were obtained in three areas: a) We have studied strained as well as annealed films of Colossal Magnetoresistance (CMR)[4-7] material (a candidate for the next generation of high density data storage devices) at various film thicknesses, and have observed that there

is more than one elastic anomaly which accompanies the CMR transition. The anomalies appear as changes of only a few percent in elastic constants in films which are only one part in 1000 of the whole sample. A paper has been written for submission to Physical Review Letters. b) We are confirming our original observation of the unexpected effect that coatings of carbon nanotubes on surfaces can reduce mechanical dissipation. A number of technologically important materials have been successfully tested, including silicon, alumina, strontium titanate, and quartz. We are investigating theories involving surface morphology by making Scanning Force Microscope (SFM) measurements. c) We have made RUS measurements on crystals of corundum (also known as alumina, a very important industrial material) and have corrected an error (made by the National Bureau of Standards) which has existed in the literature for over thirty years. A paper describing this result has been prepared for submission to Physical Review Letters.

Thin Films of Colossal Magnetoresistance (CMR) Material

Colossal Magnetoresistance is currently of great interest in physics because the effect involves an intimate interaction among electronic, magnetic, and elastic properties. A CMR material undergoes a magnetic phase transition at a critical temperature, and near this point the electrical resistance is a rapidly varying function of magnetic field, making CMR ideal for magnetic sensors in the next generation of high-density data storage devices. In the absence of a magnetic field, the CMR transition is indicated by a peak in resistance versus temperature. Most applications require CMR material in thin films, and the strain induced by lattice mismatch with the substrate alters the properties of the film; e.g., the peak resistance temperature decreases for thinner films[8-9]. Phase transitions and the effects of strain are readily detected by measuring elastic constants, and one would expect there to be some feature in the elastic constants near the CMR transition at the peak resistance temperature.

Our elastic constant measurements were the first for any CMR film. The CMR material studied was $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Fig. 2a, 2b, and 2c show results for an annealed (bulk) sample, a strained 400 nm film, and a strained 200 nm film, respectively. Each figure shows the elastic constants C_{11} and C_{44} , and the electrical resistance as functions of temperature. For each sample, there is a feature (jump and/or a change in slope) near the peak resistance temperature. However, there is also feature about 17 K higher in temperature. All features decrease in temperature as the strain increases in the thin films, tracking the peak resistance temperature. It may be speculated that a higher temperature structural change may set the environment for the magnetic transition at the lower temperature.

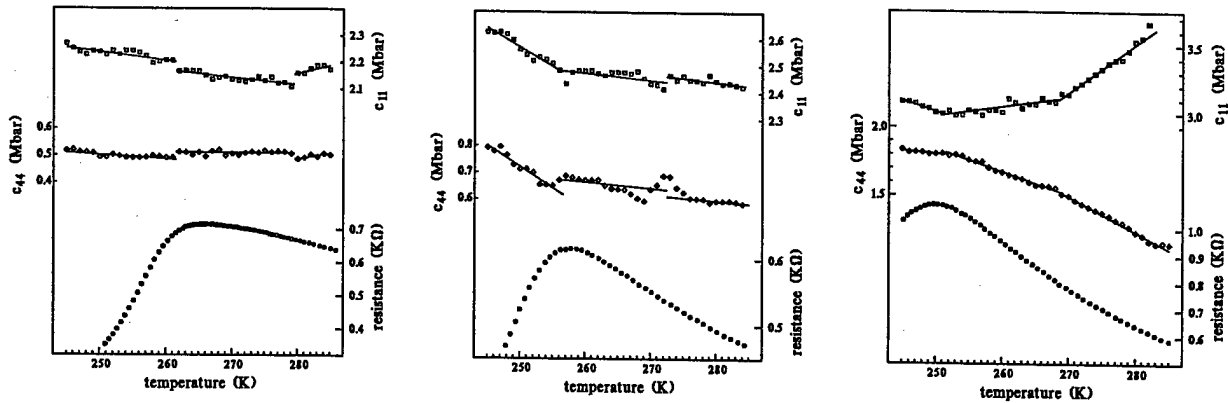


Figure 2. Results of resonant ultrasound spectroscopy measurements on a film of a colossal magnetoresistance material. a) 400 nm annealed film, b) 400 nm strained film, and c) 200 nm strained film.

Thin Films of Carbon Nanotubes

When carbon atoms are released into a controlled atmosphere, either in a carbon arc or by laser ablation, the atoms may regroup into stable clusters of 60 atoms in a "soccerball" pattern, referred to as molecular C₆₀. If certain transition metal atoms are present when the C₆₀ is trying to form, then a metal atom may chemisorb onto the rim of a half formed soccerball and prevent it from closing into a sphere. The subsequent accretion of carbon results in the growth of a cylindrical tube, which may reach a length of many microns, with a diameter as small as 1 nm. Such fibers are called single-wall nanotubes (SWNT's) and are believed to be by far the strongest fibers that can be made. SWNT fibers are essentially graphite (hexagonal) sheets rolled into tubes with hemispherical fullerene end-caps. Thin films of SWNT's may be deposited as thin films on a substrate; the SWNT's form tangled mats which bond to the substrate, probably through defects along the tube walls. It was anticipated that when the substrate moved (in bending modes, etc.) the nanotubes would slide over one another, dissipate energy, and increase damping.

Contrary to the expected result, it was found that the films of SWNT's, particularly at certain thicknesses, reduced damping. When the substrates were driven at resonance, the SWNT film caused the width of the resonance curve to be reduced (as illustrated in Fig. 3), and the quality factor (Q) to be increased, by as much as a factor of five. In our recent research, this phenomenon has been successfully reproduced on a number of technologically important materials, including silicon, alumina, strontium titanate (a common substrate for thin film research), and quartz. Other tests have shown that carbon in forms other than SWNT's do not produce the enhanced Q effect. We speculate that the SWNT enhanced Q effect results from the SWNT's bridging microcracks on the substrate surface, eliminating them as a source of dissipation; microcrack dissipation is caused by nonlinear opening and closing, converting the macroscopic vibration into thermal modes. This theory was confirmed by making Scanning Force Microscope (SFM) measurements. A patent disclosure covering a potential application was prepared.

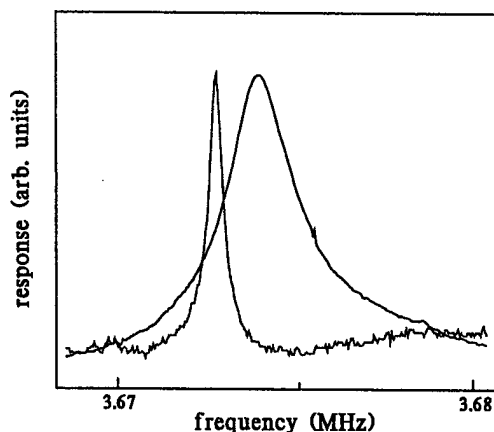


Figure 3. Illustration of the increase in the quality factor of a small mechanical resonator when a film of carbon nanotubes is deposited on a surface.

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APPENDIX

Papers published:

1. J. D. Maynard, in Proceedings of Internoise 2000, ed. D. Cassereau (International Institute of Noise Control Engineering, Paris, 2000) Vol. I, pp. 55-60. "Nearfield holography for arbitrarily shaped structures"
2. J. D. Maynard and P. S. Spoor, Handbook of Elastic Properties of Materials, ed. M. Levy, H. Bass, and R. Stern (Academic Press, NY) Vol. 2, p. 216 "Elastic properties of quasicrystals"
3. J. D. Maynard, Handbook of Elastic Properties of Materials, ed. M. Levy, H. Bass, and R. Stern (Academic Press, NY) Vol. 4 p. 140 "Acoustic properties of superfluid helium four"
4. J. D. Maynard, Rev. Mod. Phys. **73**, 401-417 (2001). "Acoustical analogs of condensed matter problems"
5. G. D. Mahan, J. R. Gladden, and J. D. Maynard, J. Appl. Phys. **90**, 4415-4422 (2001). "Acoustic shock waves in cylindrical fuses"
6. J. D. Maynard, in *Proceedings of InterNoise 2001* (2001) "Nearfield acoustic holography: a review"
7. Jin H. So, J. R. Gladden, Yufeng Hu, J. D. Maynard, and Qi Li, Phys. Rev. Lett. **99**, 036103 (2003). "Measurements of elastic constants in thin films of colossal magnetoresistance material"
8. J. H. Kinney, J. Gladden, G. W. Marshall, S. J. Marshall, J. H. So, and J. D. Maynard, J. Biomechanics **37**, 437-441 (2004). "Resonant Ultrasound Spectroscopy measurements of the elastic constants in human dentin"
9. J. R. Gladden, Jin H. So, and J. D. Maynard, Appl. Phys. Lett. **85**, 392-394 (2004). "Reconciliation of ab initio theory and experimental elastic properties of Al_2O_3 ",
10. J. D. Maynard, in *Proceedings of International Conference on Theoretical and Computational Acoustics* (2003) "A new technique combining eigenfunction expansions and boundary elements to solve acoustic radiation problems"
11. J. D. Maynard, in *Proceedings of Internoise 2003* (2003), "A new technique combining eigenfunction expansions and boundary elements to solve acoustic radiation problems"

Invited presentations:

1. Internoise 2000, August 27-30, 2000, Nice, France, "Nearfield Holography for Arbitrarily Shaped Structures"

2. Joint Meeting of the Acoustical Society of America and the Institute of Noise Control Engineering, 3-8 December, 2000, Newport Beach, CA, "Analyzing structure radiation with eigenfunction expansions"
3. Seminar, Naval Postgraduate School, Department of Physics, Monterey, CA, March 16, 2001, "Tuning-up a quasicrystal"
4. Internoise 2001, August 27-30, 2001, The Hague, The Netherlands, "Nearfield Acoustic Holography: A Review"
5. State University of New York, Buffalo, NY, Department of Physics, October 11, 2001, "Tuning-up a quasicrystal"
6. 142nd Meeting of the Acoustical Society of America, 3-7 December 2001, Fort Lauderdale, FL (co-authors J. H. So and J. R. Gladden) "A review of elastic constant measurements with resonant ultrasound spectroscopy"
7. Lecture Series, 2002 Physical Acoustics Summer School, Pacific Grove, CA, June 12-19, 2002, "Fundamentals of Physical Acoustics"
8. Invited Lecture: 144th Meeting of the Acoustical Society of America, 2-6 December 2002, Cancun, Mexico, "Reconstructing acoustic radiation using eigenfunction expansions"
9. Invited Colloquium: Los Alamos National Laboratory, National High Magnetic Field Laboratory, "Resonant Ultrasound Spectroscopy study of colossal magnetoresistance thin films", January 17, 2003.
10. International Conference on Theoretical and Computational Acoustics 11-15 August 2003, Honolulu, HI, "A new technique combining eigenfunction expansions and boundary elements to solve acoustic radiation problems"
11. Internoise 2003, 25-28 August 2003, Seogwipo, Jeju, South Korea, "A new technique combining eigenfunction expansions and boundary elements to solve acoustic radiation problems"
12. Lecture Series, 2004 Physical Acoustics Summer School, Pacific Grove, CA, June 20-27, 2004. "Solid State Properties"
13. University of Cyprus, Department of Physics, December 18, 2003, "Tuning-up a Quasicrystal".

Contributed papers:

1. A. Apostolou, J. So, Z. Lu, J. Gladden, Eliza Bradley, and J. D. Maynard The "underwater" sounds from the impact of drops in superfluid 4He *J. Acoust. Soc. Am.* **108**, 2519 (2000).

2. A. Apostolou, J. So, Z. Lu, and J. D. Maynard, "Bubble entrainment in liquid helium" Meeting of the American Physical Society
3. J. R. Gladden, Jin H. So, Rajdeep Pradhan, and J. D. Maynard, "Thin film characterization using resonant ultrasound spectroscopy", *J. Acoust. Soc. Am.* **111**, 2399 (2002).
4. Rajdeep Pradhan, Jin H. So, J. R. Gladden, and J. D. Maynard, "Using resonant ultrasound spectroscopy to study colossal magnetoresistance in thin films", *J. Acoust. Soc. Am.* **111**, 2400 (2002). 3-7 June 2002.
5. J. R. Gladden, Jin H. So, and J. D. Maynard, "Resonant ultrasound spectroscopy applied to misoriented crystals of low symmetry: corundum", *J. Acoust. Soc. Am.* **112**, 2439 (2002).
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7. Ken Pestka, J. R. Gladden, Jinhyun So, and J. D. Maynard, "A new method for measuring the elastic properties of thin films", *Bull. Am. Phys. Soc.* **49**, G32.005 (2004).

Degrees granted:

1. Antonious Apostolou, Masters Degree, August 3, 2000, *Bubble Entrainment in Liquid Helium*
2. David Chao Zhang, Ph.D., October 2001, *Stack/Heat-Exchanger Research for Thermoacoustic Heat Engines*
3. J. R. Gladden, Ph.D. Thesis, June 5, 2003, *Characterization of Thin Films and Novel Materials using Resonant Ultrasound Spectroscopy*

Other Graduate Students

1. Jin Liu (Acoustics Program)
2. Rajdeep Pradhan (Acoustics Program)

Undergraduates

1. Elisa Bradley

2. Vanessa Williamson

3. Praj Kulkarni

Post Doctoral Scholars

1. Jinhyun So

2. Zhiqu Lu

Invention disclosures:

1. J. D. Maynard and Gerald R. Mahan, March 2002 Solid Thermoacoustic Refrigerator and Power Generator

2. J. D. Maynard and J. R. Gladden, August 2002 Use of Carbon Nanotubes to Enhance the Performance of Micro-Electromechanical Systems