Final Scientific/Technical Report
DOE Award Number: DE-FG02-06ER46279
Recipient: Indiana University
Project Title: Development of new methods for studying nanostructures using neutron scattering
Principle Investigator: Roger Pynn

Executive Summary

The goal of this project was to develop improved instrumentation for studying the microscopic structures of materials using neutron scattering. Neutron scattering has a number of advantages for studying material structure but suffers from the well-known disadvantage that neutrons' ability to resolve structural details is usually limited by the strength of available neutron sources. We aimed to overcome this disadvantage using a new experimental technique, called Spin Echo Scattering Angle Encoding (SESAME) that makes use of the neutron's magnetism. Our goal was to show that this innovation will allow the country to make better use of the significant investment it has recently made in a new neutron source at Oak Ridge National Laboratory (ORNL) and will lead to increases in scientific knowledge that contribute to the Nation's technological infrastructure and ability to develop advanced materials and technologies. We were successful in demonstrating the technical effectiveness of the new method and established a baseline of knowledge that has allowed ORNL to start a project to implement the method on one of its neutron beam lines.

Comparison of accomplishments and objectives

The original hypothesis of the project was that magnetic Wollaston prisms (WP) could be used to implement SESAME and that these prisms could be realized as simple solenoids with triangular cross sections, operated at room temperature. Our goal was to build such a system and to test its applicability to a number of scientific problems where structural information is needed over a range of length scales extending from a few nm to a micron or so. We are one of five groups worldwide developing or using these methods (the other four are in Europe) and the only one to choose an implementation based on DC solenoids: all of the others use much more expensive radio frequency (rf) technologies. Since Indiana University operates a Low Energy Neutron Source (LENS) our goal was to test the WPs there and then to transfer the technology to a more powerful neutron source at Los Alamos Neutron Science Center (LANSCE). Testing at LENS was accomplished but, unfortunately, the LANSCE neutron source was closed before our equipment could be used for more than a few test experiments.

Figure 1 shows five generations of WPs, the first four of which were developed using funding from the grant reported here. The final device (Fig 1e) is being developed together with ORNL on the basis of knowledge gained through the present grant proposal and an NSF grant used to develop superconducting devices. As Fig 1a shows, our first device was extremely simple, consisting of two, triangular-cross-section solenoids yoked in a mumetal flux-return frame. We rapidly learned that this device could not work well because external magnetic fields could penetrate into the WPs and spoil the field homogeneity required for the method to work. To use these WPs effectively we would have had to enclose them in a large box within which the magnetic field was zero. While we could have pursued that route (it has been done in Europe) we chose instead a different approach shown in figure 1b. In this device, a gap is created in each triangular solenoid by bending some of its windings away from the area of the neutron beam. The gap allows the magnetic field to spill out of the solenoid and to overlap with the external guide field that maintains the neutron polarization. While the gaps produce significant non-uniform magnetic fields along the neutron beam path, we were able to show that the effects of these inhomogeneities on the Larmor phase basically cancel out because of the symmetry of the devices and off the instrument in which they are used. The gaps in the solenoids have an additional advantage that they reduce the amount of aluminum wire (used to wind the solenoids) in the neutron beam. To reach correlation lengths beyond about 200 nm we needed to cool the current-carrying wires so we built the water-cooled device shown in Fig 1c. Finally, we greatly improved the water-cooling as well as the precision of the coil winding to produce devices like that shown in Fig 1d, which had very good neutron flipping efficiency. The lessons that we learned during the development of these prisms have been shared through publications in the open literature and talks at conferences, with some of the more obscure technical details described in the PhD theses of several Indiana

University graduate students.

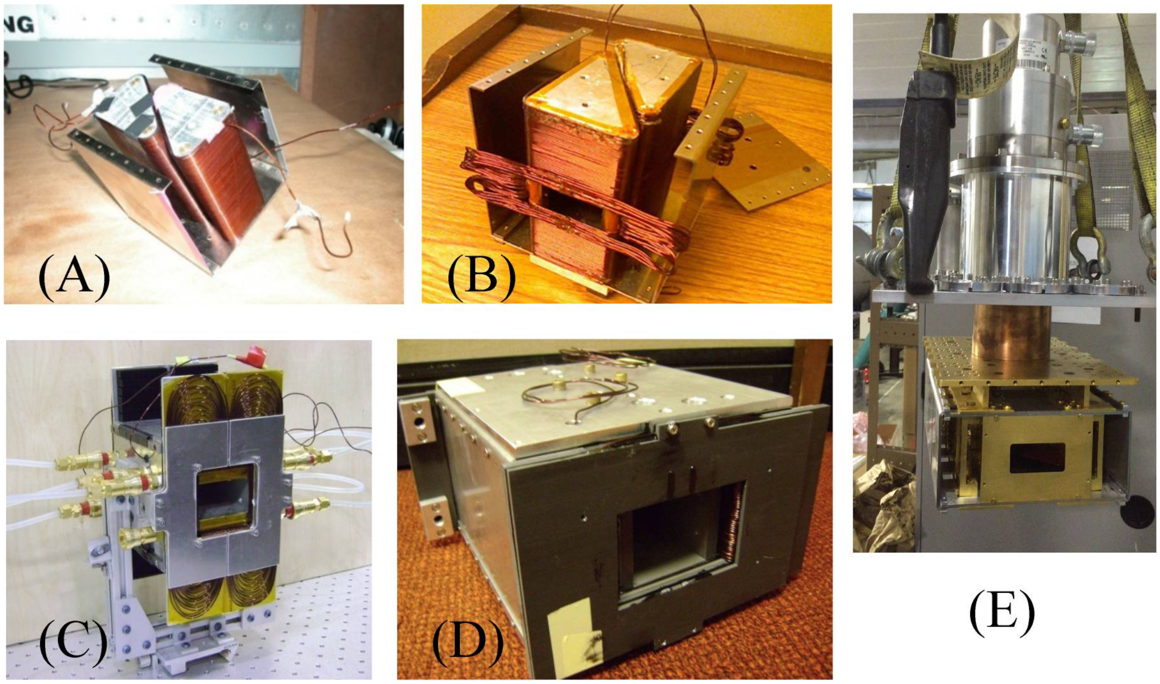

Figure 1: Sequential generations of neutron Wollaston prisms built during this project (A through D) and, more recently, in a collaboration with ORNL. Descriptions are given in the text. Each of the devices in parts A – D have side lengths between 150 mm and 200 mm.

Given that the main goal of this project was to demonstrate that DC Wollaston prisms could be used to effectively implement SESAME and to measure structural correlations over length scales between a few nm and a micron or so, this project was a success. The functional specifications we obtained for our devices are on a par with those for the much more complicated and expensive equipment installed on the instrument, OFFSPEC, constructed at the ISIS second target station at the Rutherford Laboratory in the UK. Several of the major lessons that we learned while working on this grant will be important for the future implementation of Larmor labeling techniques:

- SESAME measures a projection of the scattering-length density auto-correlation function in real space whereas most neutron scattering practitioners are used to seeing data in reciprocal space. It will take several years of seeing both types of data together for SESAME to overcome the prejudice engendered by this historical fact. The LARMOR instrument at ISIS will likely provide that experience
- SESAME is well suited to measurements of materials that scatter neutrons strongly because it measures pair correlations even in the presence of strong multiple scattering. This means that for samples available in large quantities, very fast measurements are possible, even at long correlation lengths. The corollary is that the method is NOT good for weak scatterers and many interesting samples fall into the latter category. Although we proposed to develop dark-field SESAME as part of the work done under this grant in order to address this deficiency, we did not have time to complete that task.
- While it was originally thought (by the entire community) that SESAME should be well suited for pulsed neutron sources, this conclusion has to be tempered. The statistical errors on a SESAME measurement vary strongly with neutron wavelength at a pulsed source for several fundamental reasons, implying that only a small band of wavelengths is really useful for any measurement.
- We (and others) have not been able to demonstrate a killer-app that would jump start community interest in SESAME. Absent this, the method will (like traditional spin echo before it) likely

remain a specialized technique that provides unique information in a few small niche areas.

- Using SESAME we developed a method that is functionally equivalent to grating-based holographic x-ray diffraction (see, for example, doi:10.1107/S0021889809040990) but less susceptible to errors introduced by data processing methods.
- We have realized that WPs based on what we learnt from work done on the grant will allow measurement of the lifetimes of dispersive excitations (phonons). We are currently building devices for ORNL to capitalize on this opportunity. The same devices will also support Larmor diffraction, a technique that offers an order of magnitude improvement over the best diffraction resolution obtainable at synchrotron sources. There is also a potential to use the devices to develop phase-contrast and SANS-contrast neutron radiography although, to out knowledge, no one in the US is currently working on these applications.
- SESAME produces coherent propagation of two neutron spin states that are separated in space. It is becoming clear that this is a purely quantum phenomenon and leads to the natural questions such as: what happens when spin-entangled neutrons interact with entangled electron states in matter; and, can we use this type of coherence to better probe the disordered and hierarchical structures that are of interest to modern technologies? That is, can we imagine "neutron spintronics" as a set of new methods.

Because of the shutdown of LANSCE, almost all of the scientific measurements that we performed using SESAME were done using the equipment at ISIS (in particular the instrument OFFSPEC) rather than the equipment we developed under this grant. This happened because there was no high-powered neutron source in this country where our equipment could be installed. All of our measurements have been written up and the details published. It is worth noting that the journal in which the final publication listed below (#19) will appear has requested that the authors provide an image for the front cover of the journal edition in which the work will be published.

Publications

1. The Use of Symmetry to Correct Larmor Phase Aberrations in Spin Echo Scattering Angle Measurement; Roger Pynn, Wai-Tung Hal Lee, Paul Stonaha, Shah Valloppilly, Adam Washington, Brian Kirby, Brian Maranville, and Charles Majkrzak; Rev. Sci. Instrum. **79**, 063901 (2008)
2. Spin Echo Scattering Angle Measurement at a Pulsed Neutron Source; Roger Pynn, M. R. Fitzsimmons, W. T. Lee, V. R. Shah, A. L. Washington, P. Stonaha, and K. Littrell; J. Appl. Cryst.,**41**, 897 (2008)
3. A spin-echo resolved grazing incidence scattering setup for the neutron interrogation of buried nanostructures; J. Major, A. Vorobiev, A. Ruehm, R. Maier, M. Major, M. Mezger, M. Nuelle, H. Dosch, G. P. Felcher, P. Falus, T. Keller, R. Pynn, Rev. Sci. Instrum. **80**, 123903 (2009)
4. Theoretical studies on the structure of interacting colloid suspensions by spin echo small angle scattering; X. Li, C-Y Shew, Y. Liu, R. Pynn, E. Liu, K. W. Herwig, G. S. Smith, J. L. Robinson, and W-R Chen; J. Chem. Phys., **132**, 174509 (2010)
5. Dynamical theory calculations of spin-echo resolved grazing-incidence scattering from a diffraction grating: R. Ashkar, P. Stonaha, A. L. Washington, V. R Shah, M. R. Fitzsimmons, B. Maranville, C. F. Majkrzak, W. T. Lee, W. L. Schaich, and R. Pynn; J. Appl. Cryst., **43**, 455 (2010)
6. Prospect for characterizing interacting soft colloidal structures using spin-echo small angle neutron scattering; Xin Li, Chwen-Yang Shew, Yun Liu, Roger Pynn, Emily Liu, Kenneth W. Herwig, Gregory S. Smith, J. Lee Robertson, and Wei-Ren Chen; J. Chem. Phys., **134**, 094504 (2011)
7. Scattering Functions of Platonic Solids; Xin Li, Chwen-Yang Shew, Lilin He, Flora Meilleur, Dan A. Myles, Emily Liu, Yang Zhang, Gregory S Smith, Kenneth W Herwig, Roger Pynn and Wei-Ren Chen; J. Appl. Cryst., **44**, 545, (2011)
8. Contrast Variation in spin-echo small angle neutron scattering; Xin Li, Bin Wu, Roger Pynn, Chwen-Yang Shew, Gregory S. Smith, Kenneth W. Herwig, J. Lee Robertson, Wei-Ren Chen, and Li Liu; Journal of Physics: Condensed Matter **24**, 064115 (2012)

9. Comparison of dynamical theory and the phase-object approximation for neutron scattering from periodic structures; Rana Ashkar, V. O. deHaan, A. A. VanWell, R. Dalgliesh, J. Plomp, M. R. Fitzsimmons, W. L. Schaich and Roger Pynn; J. Appl. Cryst., **44**, 958 (2011)
10. Optimization of a solid state polarizing bender for cold neutrons; V. R Shah, A. L. Washington, P. Stonaha, R. Ashkar, H. Kaiser, T. Krist and Roger Pynn; Nucl. Instrum. and Methods, A768, 157 (2014)
11. DCD USANS and Spin-Echo SANS: A comparison of two neutron scattering technqiues applicable for the study of large-scale structures; Christine Rehm, John Barker, Wim Bouwman and Roger Pynn; J. Appl. Cryst., **46**, 354 (2013)
    DOI: http://dx.doi.org/10.1107/S0021889812050029
12. Neutron Spin Evolution through Broadband Current Sheet Spin Flippers; P.Stonaha, J. Hendrie, W. T. Lee, and Roger Pynn, Rev. Sci. Instrum. **84**, 105113 (2013): DOI: http://dx.doi.org/10.1063/1.4826086
13. Inter-particle Correlations in a Hard-Sphere Colloidal Suspension with Polymer Additives Investigated by Spin Echo Small Angle Neutron Scattering (SESANS); A. L. Washington, X. Li, A. B. Schofield, K. Hong, M. R. Fitzsimmons, R. Dalgliesh and R. Pynn; *Soft Matter*, 10 (17), 3016 (2014) : DOI: http://dx.doi.org/10.1039/c3sm53027b
14. A new approach for probing matter in periodic nanoconfinements using neutron scattering; Rana Ashkar, Roger Pynn, Robert Dalgliesh, Nickolay V. Lavrik and Ivan I. Kravchenko; Journal of Applied Crystallography. **47**(4), 1367 (2014). doi:10.1107/S1600576714013387
15. Non-uniform Transmission for Supermirror Devices for Neutron Polarization; X. Tong, J. L. Robertson and R. Pynn; Nucl. Instrum. and Meth., **A768**, 77 (2014)
    http://dx.doi.org/10.1016/j.nima.2014.09.053
16. A novel Neutron Spin Echo Technique for Measuring Phonon Linewidths using Magnetic Wollaston Prisms; Fankang Li and Roger Pynn; J. Appl. Cryst., **47**,1849 (2014);
17. Thermo-responsive PNIPAM coatings on nanostructured gratings for cell alignment and release; M. Zhernenkov, R. Ashkar, H. Feng, O. O. Akintewe, N. D. Gallant, R. Toomey, T. F. Ankner and R. Pynn; ACS Appl. Mater. & Interfaces, **7** (22), pp 11857–11862 (2015)
    http://dx.doi.org/10.1021/acsami.5b01453
18. Spin echo small angle neutron scattering using a continuously pumped 3He neutron polarisation analyser: S. R. Parnell, A. L. Washington, K. Li, H. Yan, P. Stonaha, F. Li, T. Wang, A. Walsh, W. C. Chen, A. J. Parnell , J. P. A. Fairclough, D. V. Baxter, W. M. Snow, and R. Pynn Review of Scientific Instruments **86**, 023902 (2015); http://doi: 10.1063/1.4909544
19. Porosity of silica St ̈ober particles determined by spin-echo small angle neutron scattering; S.R.Parnell, A.L.Washington, A.J.Parnell, A.Walsh, R.M.Dalgliesh, F.Li, W.A.Hamilton, S.Prevost, J.P.A.Fairclough, and R.Pynn; Soft Matter (in press)

Conference Reports (presenter in bold type)

1. Using Neutron Spin Echo to probe space and time correlations in thin films; **Roger Pynn**; presented at PSI conference on surface inelastic scattering; Journal of Neutron Research, Volume 14, Issue 3, pages 221 - 227 (2006)
2. Broadband spin flippers constructed from thin magnetic films; **Roger Pynn**; presented at conference on Polarized Neutrons in Condensed Matter Investigations, Washington, DC., June 2004; Physica B356, Issues 1-4, 178 (2005)
3. Polarized Neutrons for Pulsed Neutron Sources; Ian S. Anderson, Jeremy Cook, Gian Felcher, Tom Gentile, Geoffrey Greene, Frank Klose, Tom Koetzle, Eddy Lelievre-Berna, Andre Parizzi, **Roger Pynn**, Jinkui Zhao, (Roger Pynn; Ed): J. Neutron Research, 13, 193 (2005)
4. Spin-Echo Resolved Grazing Incidence Neutron Scattering: a Neutron Resonance Spin-Echo Prototype Facility; **J. Major**, A. Vorobiev, R. Maier, M. Mezger, A. Ruhm, H. Dosch, G. P. Felcher, P. Falus, S. G. E. te Velthuis, and R. Pynn; presented at the 9th International Conference on Surface X-ray and Neutron Scattering (Taipei, 2006)
5. Suppression of nuclear polarization in photon-irradiated GaAs; **M. R. Fitzsimmons**, B. J. Kirby, F. Trouw, P. A. Crowell, C. Adelmann, S. D. Flexner, C. J. Palmstrom, M. Erickson, J. A. Borchers, C. F. Majkrzak, W. Chen, T. R. Gentile, and R. Pynn (APS March meeting, 2007)

6. A Compound Magnetic Lens for Pulsed Neutrons; **J. Suzuki**, T. Oku, T. Shinohara, H. Shimizu, and R. Pynn; presented at the International Conference on Neutron Optics, Paul Scherrer Institute, Switzerland, April, 2007
7. The Present Status of the Low Energy Neutron Source: **David V. Baxter**, A Bogdanov, V. P. Derenchuk, H. Kaiser, C. M. Lavelle, M. B. Leuschner, R. Pynn, N. Remmes, T. Rinckel, W. M. Snow, and P. E. Sokol; presented at ICANS-XVIII, Dongguan, China, April, 2007
8. A Polarizing Bender for the SESAME Beam Line at LENS; V. R. Shah, Roger Pynn, M. Leuschner and **David V. Baxter**; presented at ICANS-XVIII, Dongguan, China, April, 2007
9. Pulsed Neutron Beam Control using a Magnetic Multiplet Lens; T. Oku, T. Shinohara, **J. Suzuki**, R. Pynn, H. M. Shimizu; Nuclear Instruments and Methods A600, 1, 100-102 (2009)
10. Birefringent Neutron Prisms for Spin Echo Scattering Angle Measurement; **Roger Pynn**, M. R. Fitzsimmons, W. T. Lee, P. Stonaha, V. R. Shah, A. L. Washington, B. J. Kirby, C. F. Majkrzak, and B. B. Maranville; presented at the International Conference on Polarized Neutrons in Condensed matter Research (Mito, Japan, September, 2008); Physica B 404, 2582–2584 (2009)
11. Magnetic Vortices in Sub-100 nm Magnets; **Igor V. Roshchin**, C. P. Li, Harry Suhl, Xavier Batlle, S. Roy, S. Sinha, S. Park, R. Pynn, M. Fitzsimmons, J. Mejia-Lopez, D. Altbir, A. H. Romero, R. Dumas, Kai Liu, and Ivan K. Schuller, Proc. of International Conference on Electromagnetics in Advanced Applications, 2009 - ICEAA '09, 14-18 Sept. 2009, 1028 - 1029. DOI: 10.1109/ICEAA.2009.5297777 http://dx.doi.org/10.1109/ICEAA.2009.5297777
12. Development of a beam line for spin echo scattering angle measurement at the Low Energy Neutron Source; A. L. Washington, P. Stonaha, R. Ashkar, **R. Pynn**, V. R. Shah; Proceedings of ICANS XIX (Grindelwald, Switzerland, 2010) ISSN-Nr. 1019-6447
13. Spin Echo Resolved Grazing Incidence Scattering (SERGIS) at Pulsed and CW Neutron Sources; **Rana Ashkar**, P. Stonaha, A. L. Washington, V. R. Shah, M. R. Fitzsimmons, B. Maranville, C. F. Majkrzak, and Roger Pynn; presented at the International Conference on Neutron Scattering (2009); J. Phys.: Conf. Ser. 251, 012066 (2010); doi: 10.1088/1742-6596/251/1/012066
14. Some recent results using spin echo resolved grazing incidence scattering (SERGIS) **Roger Pynn**, Rana Ashkar, P.Stonaha, A.L.Washington; presented at Polarized Neutrons in Condensed Matter Investigation (PNCMI), Delft, (2010); Physica B406, 2350 (2011), doi: http://www.sciencedirect.com/science/article/pii/S0921452610010410
15. Dynamical Theory: Application to Spin-Echo Resolved Grazing Incidence Scattering from Periodic Structures; **Rana Ashkar**, W. L. Schaich, V. O deHaan, A. A. VanWell, R. Dalgliesh, J. Plomp, and Roger Pynn; presented at the Int. Conf. on Surface X-Ray and Neutron Scattering (SXNS11); J. Appl. Phys. 110,102201 (2011)
16. Status Report on the Low Energy Neutron Source – 2014: **David V. Baxter**, F. Li, S. R. Parnell, R. Pynn, T. Rinckel, and T. Wang; presented at ICANS XX (Mito, Japan), 2014