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Magneto-electric Energy Conversion of Optical Energy to Electricity

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In the third and final year of research on magneto-electric conversion of optical energy to electricity, several major project objectives were achieved in the areas of theory and experiment. This was chiefly the result of a breakthrough in understanding the reported enhancement of magneto-electric scattering and switching to computer codes based on Matlab to improve both the speed of computations and the time required to acquire data. On the theoretical front, a dressed state approach was successfully developed to analyze optical magnetization. The introduction of Matlab software resulted in significant speedup. Computational timescales for large matrix diagonalizations went from days to hours. Applied to atomistic models, these computations of induced dipole moments revealed that the family of nonlinearities of interest in this work arise from dynamic symmetry-breaking by the optical magnetic field.

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Abstract

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In the third and final year of research on magneto-electric conversion of optical energy to electricity, several major project objectives were achieved in the areas of theory and experiment. This was chiefly the result of a breakthrough in understanding the reported enhancement of magneto-electric scattering and switching to computer codes based on Matlab to improve both the speed of computations and the time required to acquire data.

On the theoretical front, a dressed state approach was successfully developed to analyze optical magnetization. The introduction of Matlab software resulted in significant speedup. Computational timescales for large matrix diagonalizations went from days to hours. Applied to atomistic models, these computations of induced dipole moments revealed that the family of nonlinearities of interest in this work arise from dynamic symmetry-breaking by the optical magnetic field. However they fell short of explaining the high signal intensities observed in laboratory measurements. Subsequently a molecular model was devised to exploit the idea that magnetic torque can enhance high frequency magnetic moments by transferring orbital angular momentum to rotational motion. A key advance was the realization that one can increase magnetic moments by switching from atoms to molecules and exploiting magnetic torque to increase the area enclosed by librating charges. Progress on a semi-classical version of the theory showed that this concept had all the key features needed to explain experimental intensities, but development of a fully-quantized version of the theory proved to be very challenging. The exact version of the theory was not completed before the end of the award. Nevertheless work during this grant period established both the universality of magneto-electric (M-E) nonlinearities and the key role played by rotational dynamics.

On the laboratory front, a major effort was made to improve signal-to-noise by automating data acquisition. Software was developed to control the drivers for mechanical rotation mounts and other optics involved in recording radiation patterns from scattering experiments. The first observations of cross-polarized signals and unpolarized background scattering in C_6H_6, C_6D_6, ethylene glycol, a viscous hybrid material (phenylsilsesquioxane: dimethylsiloxane), analine, benzonitrile, YAG and GGG were made subsequently. A comparison of deuterated and un-deuterated benzene permitted us to reach a milestone by verifying the importance of rotational frequencies in enhancing magnetic scattering. The ratio of magnetization slopes of these compounds agreed with the ratio of their (squared) moments of inertia. This provided theoretical confirmation that molecules as opposed to atoms have unique advantages for energy conversion applications.

1. Review of Research Objectives

This program undertook an initial investigation of processes relevant to optical energy conversion based on magneto-electric rather than photovoltaic processes. The research built on

prior experiments and theory suggesting that a battery-like charge separation is produced by passing light through transparent insulating solids to realize a novel energy source in the form of an "optical capacitor". In principle such a process can evade key limitations of other energy conversion schemes, particularly thermodynamic limitations. The heat load accompanying magneto-electric rectification was theorized to be negligible, since the conversion process involves a field effect. As a result, optical-to-electrical efficiency was predicted to be high, possibly exceeding the theoretical performance of current semiconductor-based photovoltaic cells illuminated by sunlight. By formulating an exact approach to the theory of M-E nonlinearities, it was confirmed during the final year of research that the efficiency should approach the Landsberg limit, close to unity. Quantitative comparisons of magneto-electric response were performed with partial success in identifying guidelines for future efforts to harness M-E energy conversion concepts and technology.

2. Timetable & Research Topics

Table 1. Proposed Research Schedule

Year	**1**				**2**				**3**			
Quarter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Magnetic scattering comparisons of standard reagents; deduction of ME saturation intensities	*	*	*	*	*	*	*	*				
Test frequency & polarization dependence of magneto-electric nonlinearities; radiation patterns					*	*	*	*	*	*	*	*
Compare MD scattering intensities & charge separation in EO & centro-symmetric solids			*	*	*	*	*	*	*	*	*	*
Measure SHG vs input power					*	*	*	*				
Correlate electrical detection of ME rectification with SHG intensities vs power					*	*	*	*	*	*	*	*
Confirm generation of THz signals in unbiased samples; measure Cerenkov angle							*	*	*	*	*	*

3. Progress of the Research Effort

Year 3:

During the final report period research progressed on three main fronts: quantum theory of magneto-electric nonlinearities, elastic scattering experiments and the search for charge separation. Progress on these topics has maintained a pace close to the anticipated schedule (Table 1), and is summarized in the respective sections below.

3.1. Experiments

3.1.1. Elastic Light Scattering

In Year 3, the experimental effort in light scattering focused on the need for quantitative comparisons between various materials available to the project through commercial suppliers or through collaborations. The need to advance material comparisons was hampered by the

unexpected finding that many samples did not exhibit a cross-polarized signal in the radiation pattern. Since the ratio of cross-polarized scattering to co-polarized (Rayleigh) scattering is the only basis available at present for scattering-based comparisons of M-E properties, this represented a significant hurdle.

Benzene is a case in point. No polarized component was observed in benzene in any recent experiments. This means that our proposed method of comparing magneto-electric properties of benzene with that of our reference liquid CCl_4 cannot be implemented. In CCl_4, polarized and unpolarized components are consistently observed together in the cross-polarized signal (as shown in Fig. 1). In contrast to this we found only one of the two components in the majority of organic compounds studied, forcing us to devise a different strategy, as follows. Since the intensity dependence for both components was quadratic in CCl_4, it is reasonable to assume both are of magneto-electric origin. For some materials it may therefore be possible to use the intensity dependence of the unpolarized component first to establish that the scattering is indeed magneto-electric in origin and second to make useful M-E material comparisons based on observations of this component.

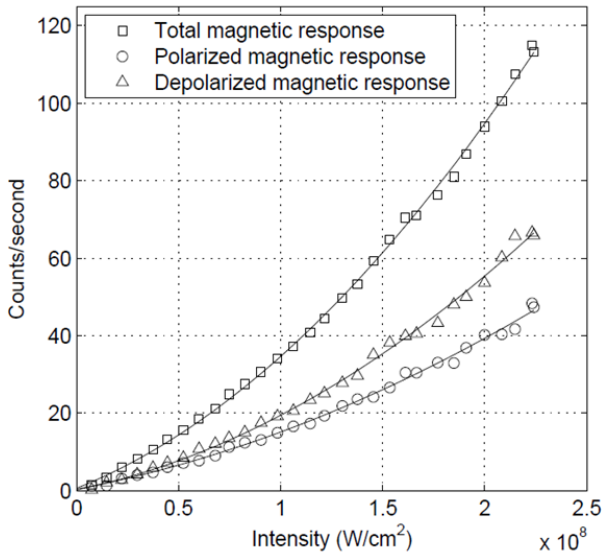

Figure 1. Quadratic intensity dependence of cross-polarized scattering in CCl_4.

An important caveat in this strategy is that it must be known that no other mechanism can give rise to cross-polarized scattering. In CCl_4 other depolarizing mechanisms are eliminated from the start by the considerations that the molecule is non-chiral, the liquid is centrosymmetric, and there is no permanent dipole on the molecule, etc. In benzene the situation is regrettably different. Benzene is anisotropic. Therefore anisotropic polarizability can be induced and depolarization may take place by a third order all-electric torque interaction [1]. Thus the cross-polarized scattering observed in benzene may be complex in origin, arising from more than just the magneto-electric process of interest. It could also originate from electric torque, so studies over a wider range of intensity are mandated. A major advance is simply to have observed that the depolarization ratio in benzene and other liquids is intensity-dependent, a result not reported in early scattering experiments [2].

New scattering experiments were completed in samples of C_6H_6, C_6D_6, ethylene glycol, a transparent hybrid (phenylsilsesquioxane:dimethylsiloxane), analine, benzonitrile, YAG and

GGG in Year 3, but the overwhelming majority of experiments on organic materials did not exhibit well-defined polarized signals of the type needed to make meaningful material comparisons. With improved signal-to-noise it may yet be possible to observe this component. However, failing that, it is possible that low intensity observations may be needed to verify that the unpolarized scattering is quadratic and useful in its own right. As an illustration of this, consider the data of Figure 2. In the right panel, data for different materials increases at different rates. It is interesting to note that the slopes for C_6H_6 and C_6D_6 are consistent with the squared ratio of their moments of inertia, just as expected if the scattering were attributable to M-E interactions. With suitable evidence that this data is dominated by the M-E nonlinearity of interest, this isotope effect could directly confirm the dependence of magnetization on rotational frequency. However for the time being a more definitive conclusion must await improved signal-to-noise in the scattering experiments.

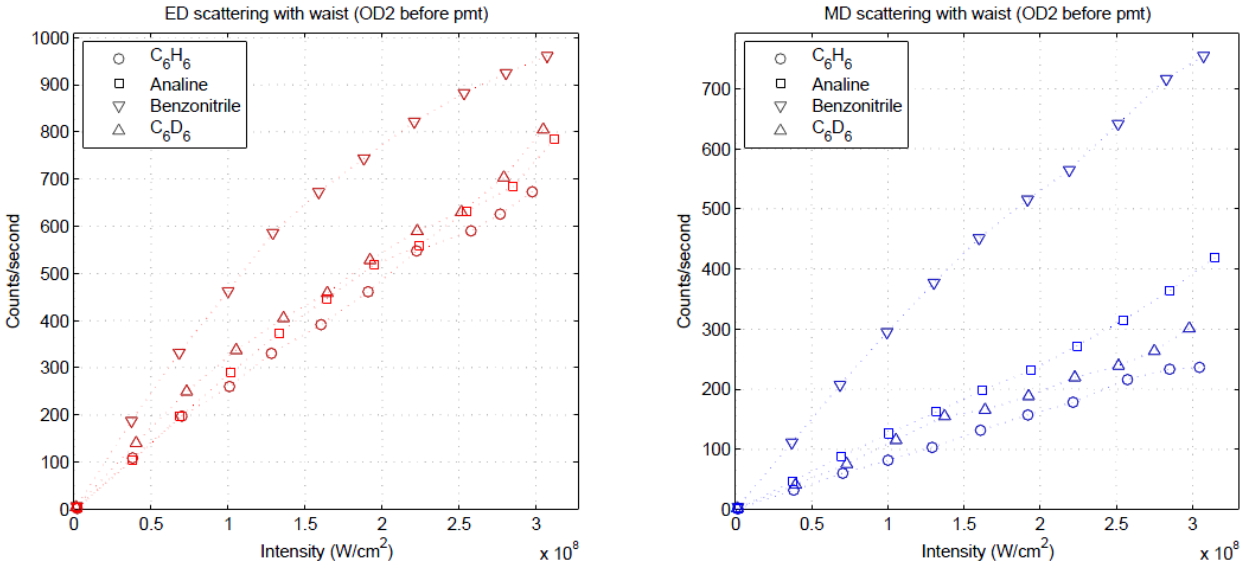

Figure 2. Co-polarized (left) and cross-polarized (right) scattering signals versus input intensity for four liquids. Provided the cross-polarized responses reflect magneto-electric interactions rather than some other interaction, the conclusion can be drawn that the medium with the highest slope has the largest M-E susceptibility.

The suggestion that improvements in signal-to-noise could be valuable is supported by the data of Figure 3. In these plots, the co-polarized and cross-polarized radiation patterns from experiments in a garnet crystal are displayed. While the raw data on the left has a very large unpolarized background, there is clearly a polarized component that can be extracted, because here the signal-to-noise is sufficient to do so. The polarized components derived by subtracting the waist are re-plotted on the right and serve to emphasize the importance of improving data acquisition and extracting small contributions.

The plots on the right provide an additional, unprecedented result, a milestone for this project. They show that in solid GGG, where anisotropic polarizability does not exist to compromise the interpretation that the solid dots arise from magnetic scattering, the intensity of MD scattering rivals that of Rayleigh scattering (open circles). This is the result of enhancement by a factor greater than the inverse square of the fine structure constant. It is the highest relative

intensity of cross-polarized scattering recorded in any material to date, and suggests that solids may be inherently excellent M-E materials. A possible interpretation of this result is that the effective moment of inertia for liberating charges in crystals is high, resulting in an especially low detuning of the 2-photon transition that generates the magnetic moment.

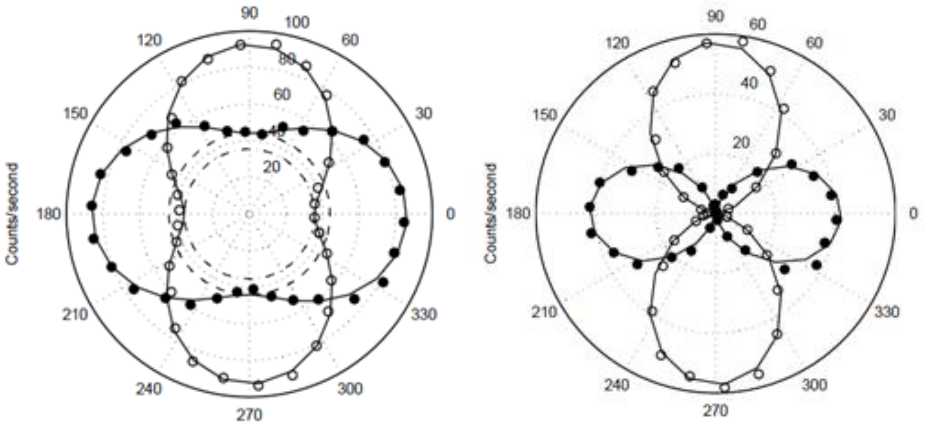

Figure 3. Left: Radiation patterns for co-polarized (open circles) and cross-polarized (filled circles) quasi-elastic light-scattering in Gadolinium Gallium Garnet (GGG). Right: Same data as on the left, with the unpolarized background contribution removed. Note that the maximum radial extent of open and filled circle data is comparable.

The experimental results above were obtained after revising our data acquisition was protocol. A control program based on valid code was found to halt operation at random times, a problem initially attributed to incompatibility between the laboratory version of Labview software and driver requirements for the new rotary stages. However the problem persisted with updated versions of the software. Consequently a completely new program was implemented using Matlab to permit radiation patterns to be recorded with greatly improved averaging and referencing and automated intensity control of the laser for weeks at a time. Since its introduction, this program has performed flawlessly.

3.1.2. Experiments on Charge separation (M-E Rectification)

During the last year of the program we sought to observe voltages on small transparent electrode structures formed as parallel plate capacitors on silica samples. To match capacitor area to the spot size of a focused Ar laser, micro-deposition techniques were employed in the facilities of the Lurie Nanofabrication lab at UM. A photo of the energy conversion testbed is shown in Figure 4 and the miniature capacitor structures deposited on glass are shown in Fig. 5. By simply chopping the incident laser beam and detecting synchronous voltages from the samples, searches were performed for optically-induced signals. Large signals were indeed recorded for the smallest structures. However these proved to be thermo-electric in origin, arising because of excessive optical absorption in the nominally transparent InSnO electrodes. Furthermore estimates revealed that even focused cw Ar^+ laser power at the 1 Watt level was inadequate to produce a saturated M-E response as needed. Hence higher optical intensity or on-chip pre-amplification is necessary for this approach to work. Additionally it was realized that unpumped areas of "optical capacitors" have the potential of forming ground return paths that

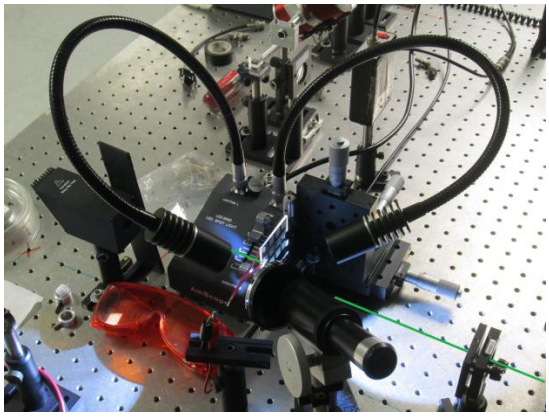

Figure 4. Testbed for measuring longitudinal voltages induced across silica glass samples by an incident Argon laser beam (in green). Measurement structures are shown in Figure 5.

nullify energy extraction. So great care is needed in matching illumination to the electrode structures. A second generation experiment has been designed using applied optical fields from a mode-locked Ti:sapphire oscillator. This should solve the need for higher intensities, reduce the heat load from parasitic light absorption by approximately five orders of magnitude, and simultaneously provide accurate control of focusing.

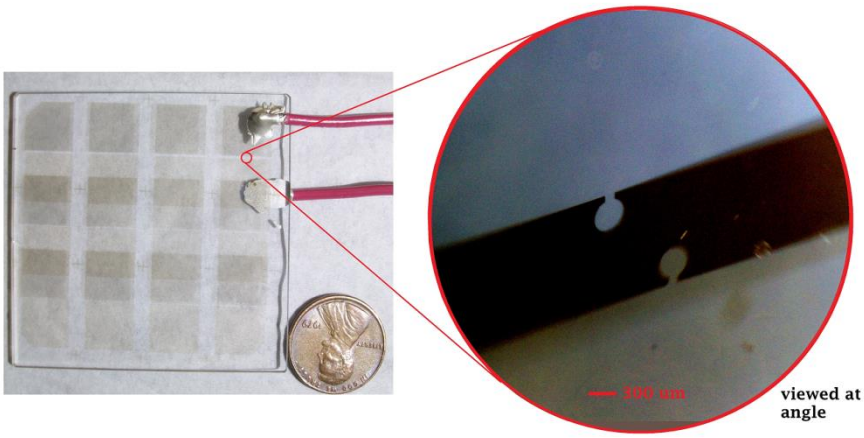

Figure 5. Micrograph of circular electrodes deposited next to large sensor soldering pads. The incident laser was focused to a spot size that matched the area of the miniature capacitor.

A first experiment on symmetry-breaking was devised and built to search for induced birefringence in a crossed field geometry (see Fig. 6 below). The experiment was motivated by the idea that charge separation should induce detectable birefringence in samples irradiated by intense laser light, with an optical axis parallel to the propagation axis. A highly-polarized probe beam was sent through a transverse (quasi-static) magnetic field region where a longitudinal electric field was present. Polarization of the probe was adjusted to be 45^0 with respect to the magnetic field axis and a longitudinal electric field of ~100 V was applied to the sample (1x1x1 cm^3 fused silica). In the presence of synchronously-modulation of the electric and magnetic fields, evidence was sought for induced transmission through a crossed polarizer, indicative of the expected, parity-violating interaction. The apparatus was designed to exploit the ease with

which large, quasi-DC electric and magnetic fields can be produced in the lab and to mimic strong optical field effects calling for high power ultrafast pulses at very low frequencies. However this first experiment was thought to yield a null result because the energy conversion by charge separation is predicted to be proportional to the modulation frequency of the fields. The speed of current modulation with our fastest high current amplifier was limited to 1 kHz which is a factor of 10^8 lower than achievable with a mode-locked laser source. Hence while this experiment attempted to capitalize on simple ways to generate large field strengths, future versions of it will exploit the high repetition rate from our newly acquired mode-locked Ti:sapphire laser.

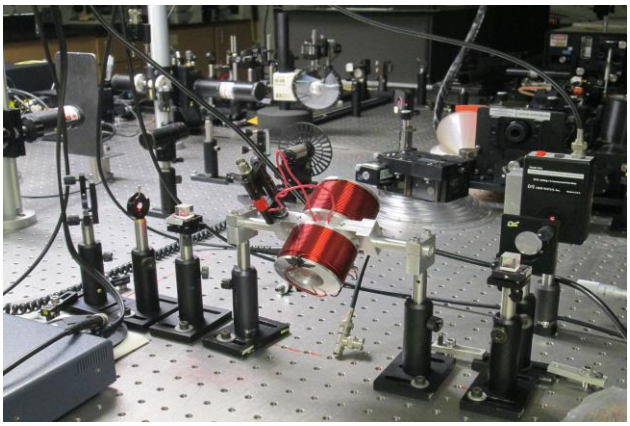

Figure 6. First version of a magneto-electric symmetry-breaking experiment. The sample (fused silica) is in the center of the photo between crossed electric and magnetic fields that are modulated synchronously at 1 kHz. Estimated field strengths were $E \approx 10^4 V \cdot m^{-1}$ and $B \approx 10^{-1} Tesla$.

3.2. Progress on Theory

In Year 3, two important breakthroughs were made on theoretical issues. The first was the realization that magnetic torque exerted by the magnetic field plays a crucial role in magneto-electric effects. The second was that rotations generated by the 2-photon transition that drives optical magnetization and charge generation affect the theoretical efficiency of "optical capacitors".

It is widely appreciated among researchers interested in high-frequency magnetism that atoms are small and can only support charge circulation within the small confines of the atom. Hence it stands to reason that larger systems are needed to support larger dynamic magnetic moments, which ought to scale as the area available for charge circulation. Molecules may therefore be inherently better systems for magnetic response at high frequencies than atoms. Moreover the magnetic torque $\overline{L} \times \overline{B}$ that light is capable of exerting on the angular momentum *L* of an excited molecule can couple the high-energy-small-area moments of constituent atoms to the low-energy-large-area librational moments described by angular momentum *O* of molecules (Figure 7). The estimated transfer time of angular momentum between *L* and *O* is not only ultrafast but it can account for experimentally-observed magnetic scattering.

The enhancement of magnetic moments by torque dynamics is enough to account in principle for the intense MD scattering reported during this project. More important still, the 2-

photon transition responsible for transverse magnetization creates rotation of the molecule which contributes some heating to the system. While not significant in the context of magnetization, this finding sets a limit on the theoretical efficiency of "optical capacitors". For each incident photon roughly one quantum of rotation is created, for an efficiency governed by the ratio of the corresponding frequencies, or $\eta = (\omega_0 - \omega_\phi)/\omega_0 \approx 0.999$.

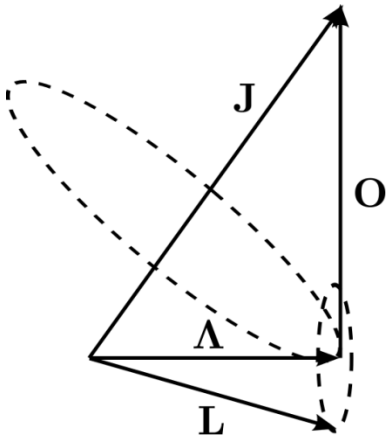

Figure 7. Diagram of the total angular momentum *J* of a molecule, consisting of an orbital part *L* and a rotational part *O*. The magnetic field of light couples these two degrees of freedom in a way that allows internal rotations with small areas to couple to external rotations with large areas (and correspondingly large magnetic moments).

4. Results Summary

4.1. Milestones

1. Radiation Patterns – Automated acquisition and extraction of two co- and two cross-polarized scattering components achieved using elastic light scattering
2. Depolarization ratios - found to depend on incident power levels
3. Material Comparisons – Molecules with large moments of inertia and crystals achieved magnetic saturation at the lowest intensities.
4. Efficiency Limit –Thermodynamic limit of energy conversion efficiency estimated from heat generated by rotational excitations to be $\eta \approx 0.999$, very close to unity and much higher than the limits of photovoltaic technology

4.2. Students Supported

Elizabeth Dreyer (Ph.D.)
Alex Fisher (Ph.D.)
Michael Purcell (Ph.D.)
Bradley Smith (Ph.D.)
Hope Wilson (UG)
Max Zeitlin (UG)

4.3. Publications:

(See attached list)

5. References

1. P.D. Maker and R.W. Terhune, Phys. Rev. 137, A801(1965).
2. H.Z. Cummins and R.W. Gammon, Appl. Phys. Lett. 6, 171(1965).

RAND_FA9550_12_1_0119_Cumulative Publications

Journal Articles

1. A.A. Fisher, E.F. Dreyer, W.M. Fisher, and S.C. Rand, "Dynamic Symmetry-breaking in a simple quantum model of magneto-electric rectification, optical magnetization, and harmonic generation", Optics Express 22, No. 3, 2910(2014).

1. A. Fisher, E. Cloos, A. Chakrabarty, and S.C. Rand, "Transverse Optical Magnetization in Crystals", Physical Review Letters (under review).

2. A. Fisher, A. Chakrabarty, E.F. Dreyer, and S.C. Rand, "Magneto-electric Nonlinearities: Theory and Experiments", Physical Review A (in preparation).

Conference Papers:

E. Cloos, A. Fisher, W.M. Fisher and S.C. Rand, "Experiments & Analysis of Second-order Magnetization in Centrosymmetric GGG Crystals", Frontiers in Optics (FiO'13), Annual Meeting of the Optical Society of America, Orlando, Florida, Paper LTu1H.1 (2013).

S.C. Rand, E. Cloos, A. Fisher, and W.M. Fisher, "Induced Magnetic Scattering in Non-Magnetic Solids", Nonlinear Optics (NLO'13), Topical Meeting of the Optical Society of America, Hawaii, Postdeadline Paper PTh3A.7 (2013).

A.A. Fisher, E. Cloos, B. Smith, A. Chakrabarthy, J. Whitaker and S.C. Rand (invited), "Intense Magnetic Optical Nonlinearities – the Emerging Story", International Conference on Luminescence, Wroclaw, Poland, July 13-18 (2014).

Books in Preparation:

S.C. Rand, "*Lectures on Light: Nonlinear and Quantum Optics using the Density Matrix*", Second Edition, Oxford University Press.

Invited Presentations

1. S.C. Rand, "New Frontiers of Nonlinear Optics", Meeting of the Optical Society of America (Ann Arbor Chapter), Dec. 11, 2012.

2. S.C. Rand (Distinguished Speaker) "Optical Magnetism: An Anecdote on Discovery in the 21st Century", Indian Institute of Technology Kharagpur, India, January 16 (2014).

3. S.C. Rand, "Optical Magnetism: An Anecdote on Discovery in the 21st Century", S.N. Bose National Center for Basic Sciences, Kolkata, India, January 13 (2014).

4. S.C. Rand, "New Science for Solar Energy?", Dept. of Physics, Indian Institute of Technology Delhi, India, January 22 (2014).

5. S.C. Rand, "Optical Magnetism: Sustained Science for Sustainable Energy", College Colloquium, Amity University, Haryana, India, January 23 (2014).

6. S.C. Rand, "Sustainable Energy from Optical Magnetism?", Dept. of Physics, University of Canterbury, Christchurch, New Zealand, April 4 (2014).

7. S.C. Rand, "Optical Magnetism for Solar Energy?", Quantum Condensed Matter Research Group, Center for Emergent Matter Science, RIKEN, Tokyo, Japan, April 28, 2014.

8. A.A. Fisher, E. Cloos, B. Smith, A. Chakrabarthy, J. Whitaker and S.C. Rand (invited), "Intense Magnetic Optical Nonlinearities – the Emerging Story", International Conference on Luminescence, Wroclaw, Poland, July 13-18 (2014).