Photoinduced magnetism (PIM) studies were successfully extended to the class of organic-based high Tc magnetic semiconductors based on V[TCNE]₂, with PIM discovered in the chemical vapor deposition (CVD) prepared films to nearly 150 K. A previously unknown phenomenon, photoinduced diamagnetism (reversible decrease in the magnetization) was revealed in these materials. We developed a powerful new experimental method to studies PIM, Photoinduced Ferromagnetic Resonance (PIFMR). PIFMR determined that the photoinduced decrease of the magnetization of V[TCNE]₂ was due to a photoinduced reduction in the permeability of V[TCNE]₂ and did not affect the saturation magnetization of the V[TCNE]₂. Thus photomodulation of the permeability of antenna materials incorporating V[TCNE]₂ may be possible. Vₘₙ[TCNE]₂ z(CH₂Cl₂) samples, with M = Co, Fe were prepared in solution of CH₂Cl₂ to further control the permeability and PIM. Modification of the CVD reactor to prepare films with three components (e.g., V(CO)_₆, Co₂(CO)₈, and TCNE are being made. These modifications must accommodate the different vapor pressures and reactivity rates for the different components. When these modifications are complete this will be a powerful means to prepare films for future PIM development as well as for preparation of three component films for incorporation in multilayers for controlled permeability.
**Executive Summary:**

**Progress and Accomplishments**

During the Period of AFOSR Grant No. F49620-03-1-0175

The support of AFOSR (since 1 December 1999) has been instrumental in the exciting and rapid progress in our investigations of the phenomenon of photoinduced magnetism. Our research has resulted in major publications, invited and contributed talks. It has received notable recognition from the scientific community, as well as attention of a wider audience, reflected in numerous popular articles featuring our work. A list of publications, presentations, and articles in popular press that have resulted from the studies under the AFOSR grant is presented below. The materials presented here represent the advances made in the grant period, i.e., March 1 2003 through February 28, 2006. The project has been a combination of synthesis, characterization, and photoinduced magnetism studies.

Remarkable progress was achieved in our investigations of photoinduced magnetism (PIM) in several families of molecule-based magnets during the first three years of AFOSR support (1999-2002). These include development of a new experimental method to studies PIM (the first report of photoinduced ac susceptibility (PIACCHI)), report of the first system with coexisting photomagnetic and spin glass behavior, proposal of a new mechanism for photomagnetic effects in Prussian blue magnets, and, discovery of the first organic-based light-modulated magnet. We determined a highly unconventional type of magnetic ordering and proposed the first model for PIM effects that accounts for the observed cluster glass behavior. Our discovery of PIM in Mn[TCNE]₂₂(=CH₂Cl₂) (TCNE = tetracyanoethylene) resulted in dramatically higher PIM operating temperature (~ 80 K) than the one for the initially studied Prussian Blue magnets (~ 20 K).

During the second three-year funding period (2003-2005), PIM studies were successfully extended to the class of organic-based high Tₛ magnetic semiconductors based on V[TCNE]₂, with PIM present in the chemical vapor deposition (CVD) prepared films of nearly 150 K. A previously unknown phenomenon, photoinduced diamagnetism was discovered in these materials. That is, the PIM resulted in a reversible decrease in the magnetization of these materials. We developed a powerful new experimental method to studies PIM in V[TCNE]₂ and related materials, PhotoInduced FerroMagnetic Resonance (PIFMR). PIFMR demonstrated that the photoinduced decrease of the magnetization of V[TCNE]₂ was due to a photoinduced reduction in the permeability of V[TCNE]₂ and did not affect the saturation magnetization of the V[TCNE]₂. This opens the possibility of using the PIM phenomenon to photomodulate the permeability of antenna materials incorporating V[TCNE]₂. During this second three year funding period studies were carried out to use chemistry to further control the permeability and PIM of the V[TCNE]₂ family. VₓM₁₋ₓ[TCNE]₂₂[CH₂Cl₂] samples, with M = Co, Fe were prepared in solution of CH₂Cl₂. Similar to solution prepared samples of the V[TCNE]₂ PIM was not observed in these samples. Work has begun in modification of the CVD reactor to prepare films with three component (e.g., V(CO)₅, Co(CO)₅, and TCNE). These modifications must accommodate the different vapor pressures and reactivity rates for the different components. When these modifications are complete this will be a powerful means to prepare films for PIM as well as for preparation of three component films for incorporation in multilayers. Selected detailed results for study of PIM of V[TCNE]₂ CVD prepared films are shown below.

The experiments during the second three year funding period included the first use of ac susceptometry to probe light induced changes in spin dynamics in RbMn[Fe(CN)₅]₅ where light can be used to switch from a diamagnetic state to a ferromagnetic state. Selected results are shown below. In the past year we also successfully discovered and characterized the PIM in a class of material, the pentacyano Prussian Blue analogue Cr[Cr(CN)₃NO], with Tₛ = 80 K and positive PIM present to ~ 50 K. Results are illustrated below for this new system.

We also carried out extensive syntheses and chemical, magnetic, and PIM characterization of several new classes of materials that, because of their chemical and crystal structures were expected to possibly show PIM. The materials included VₓCo₁₋ₓ[TCNE]₂, x = 0.25, 0.5, 0.75, Mn[TCNQ]₂, Ni[TCNQ]₂, Mn[TCNE]₂, from MnI₂, and [RuIII(CO)₂(O₂CCH₃)₂]₂[Mo(VI)(CN)₆], M = Co, Fe, Ni, Cr in H₂O, and M = Co, Fe, Cr in CH₃CN. Unfortunately no or only weak PIM was determined in these materials. Further studies are in progress to determine if the PIM is truly absent or is suppressed because of the fabrication method used. Detail data were provided in an earlier powerpoint report provided in August 2005 to Dr. Charles Lee, and reproduced in Appendix A.

A new room temperature organic-based magnet was prepared in solution using V(CO)₅ and tetracyanobenzene (TCNB). V[TCNB]₃ forms powders with magnetic order up to 325K, only the third molecule-based magnet with magnetic ordering above room temperature, see below, and the PIM will be the subject of future studies.
Selected recent results (more extensive results were sent as powerpoint files to Dr. Charles Lee in August 2005 and are reproduced in Appendix A).

Initial studies of the photoinduced magnetism (PIM) of powder samples of the room temperature magnet $\text{V[TCNE]}_2$ made from $\text{CH}_2\text{Cl}_2$ solution (and incorporating solvent) did not produce observable PIM. We extended the studies to PIM for chemical vapor deposition (CVD) prepared solvent-free films, achieving PIM success. The CVD films prepared are magnetic to above room temperature. Excitation with 458 nm light the $\pi - \pi^*$ transition of TCNE (Fig. 1) gives a reversible ~15% modulation of the magnetization at low temperature, that persists to ~150 K, Fig. 2, together with reversible photoinduced changes in the hysteresis loop. Fig. 3. The PIM in $\text{V[TCNE]}_2$ differs from that of $\text{Mn[TCNE]}_2$. For the $\text{Mn[TCNE]}_2$, the PIM is in the form of a light induced increase in the magnetic response of the $\text{Mn[TCNE]}_2$ powder. For $\text{V[TCNE]}_2$, the PIM is in the form of a light induced decrease in the magnetic response of the $\text{V[TCNE]}_2$ film.

Extension of these PIM studies to solution made powders incorporating Co and other ions were not successful at increasing the temperature for the PIM. (We note that the solution prepared powder samples of $\text{V[TCNE]}_2$ also did not show PIM, thus there is an important role for the preparation technique in achieving PIM.)

We are in the process of modifying our CVD chambers to allow more complex compositions to be prepared by this method. The potential impact of these results extends beyond light control of magnetism of $\text{V[TCNE]}_2$ films. In parallel studies we recently have been successful in showing that $\text{V[TCNE]}_2$ is a fully spin polarized magnetic semiconductor that may be incorporated as a spin analyzer layer in spin valve structures. Our PIM results support the possibility of, for the first time, using light to control spintronics. Further, our earlier studies showed the potential of using $\text{V[TCNE]}_2$ pellets to guide magnetic fields. The PIM effect in $\text{V[TCNE]}_2$ films may enable using light to control the behavior of antennas incorporating $\text{V[TCNE]}_2$ as a magnetic component.

We have extended our study of PIM of $\text{V[TCNE]}_2$ CVD films to the study of the effect of light on the X-band ferromagnetic resonance, FMR, Fig. 4 We find that excitation into the $\pi - \pi^*$ absorption results in an increase in the EPR linewidth and a decrease in the resonance field. At the same time there is no significant change in the
integrated EPR intensity, Fig. 5. This demonstrates that the PIM results as shown in Fig. 2 are a result of photoinduced changes in permeability and not changes in the saturation magnetization. This supports the potential utility of PIM in V[TCNE]₂ and similar materials for optical control of antenna function.

We have extended our studies of PIM in the M[TCNE]₂ family to solution prepared powders of VₓCo₁₋ₓ[TCNE]₂ z(CH₂Cl₂), which enable us to control coercivity of the material. The solution made Co[TCNE]₂ z(CH₂Cl₂) does not show magnetic ordering and is paramagnetic as the temperature is reduced to 2 K. Partial substitution of V with Co in V[TCNE]₂ z(CH₂Cl₂) introduces an addition disorder. While maintaining a Tc above room temperature and providing a means to chemically control the coercive field, the solution made powders did not show a PIM. Work is in progress to develop the means for deposition by CVD films of VₓCo₁₋ₓ[TCNE]₂.

Recently we extended the classes of materials with PIM to...
the pentacyano Prussian blue analogue Cr[Cr(CN)₅NO], Fig. 6, with Tₑ = 80 K yields positive PIM present to ~ 50 K, Fig. 7. This illustrates that PIM is possible in a wide range of materials systems yielding many opportunities for optimization.

Figure 8 shows the magnetization vs. temperature for V[TCNB]ₓ·yCH₂Cl₂ powders, illustrating that this is a new family of room temperature organic-based magnets (Tₑ = 325 K). We will be studying PIM of powders and modifying our techniques for CVD preparation of V[TCNB]ₓ films. We also will develop techniques for mixed organic-based magnets, e.g., V[TCNE]ₓ[TCNB]₁ₓ. Organic acceptors tetracyanobenzene (TCNB) and tetracyanoethylene (TCNE) are illustrated in Fig. 9. Both TCNE and TCNB are spinless when neutral. They are both good acceptors and when having a minus 1 charge have the charge delocalized on the acceptor with associated spin one-half. Having a 'mixed' organic lattice

[TCNE]ₓ[TCNB]₁ₓ will lead to mismatch of their valence and conduction bands, resulting in higher electrical resistivity and therefore reduced eddy current losses. It is noted that mixed metals (e.g., Fe substituted for some of the V) also may be made to simultaneously control the coercive field and permeability as well as substitution of some of the TCNE by TCNB or analogs to control resistivity and loss.

Fig. 7 PIM of Cr[Cr(CN)₅NO] to 50 K.

Fig. 8 M vs T for V[TCNB]ₓ·yCH₂Cl₂.

Fig. 9 TCNB (above) and TCNE (below).
**Personnel Supported:**
List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

**PI and Co-PI**
Arthur J. Epstein (PI)
Joel S. Miller (Co-PI and subcontractor)

**Graduate Students:**
Bretni Kennon (University of Utah)
Kendric Nelson (University of Utah)
Michelle Taliaferro (University of Utah)
Laura Turnbow (University of Utah)
Jung Woo Yoo (Ohio State University)

**Postdocs:**
Joshua Bagnato (University of Utah)
Chen Liu (University of Utah)
Kil Min (University of Utah)
Joshua Moore (University of Utah)
Thomas Vos (University of Utah)
P. Raju Nandyala (The Ohio State University)

**Peer-Reviewed Publications citing AFOSR support (2003-2006)**


Press Articles Citing Research Supported by AFOSR (2003-2006):


Presentations supported by AFOSR

Invited Talks presented at National and International Meetings:


A.J. Epstein, Organic-Based Magnetic and Non-Magnetic Semiconductors for Spintronics, Sixth International Topical Conference on Optical Probes of Conjugated Polymers and Biosystems, Bangalore, India, January 4-8, 2005.


A.J. Epstein, *Photoinduced Magnetism In Molecule-Based Magnets*, AFOSR Polymer Chemistry and Polymer Matrix Composites Program Reviews, San Diego, California, August 8-13, 2005.


**Contributed Talks Presented at National and International Meetings:**


Seminars and Colloquia:


A.J. Epstein, *Organic-Based Magnets*, Society for Physics Students Seminar, Physics Department, The Ohio State University, Columbus, Ohio, February 10, 2004.


