EPR Study of Strain-Mediated Photoeffects in Core-Shell Prussian Blue Analogues

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Introduction

The Prussian blue analogue $A_iCo[Fe(CN)_6]_j \cdot nH_2O$ (CoFe) is known to exhibit persistent photoinduced magnetism (PPIM) at temperatures below 20 K [1]. Heterostructures of CoFe with another analogue, $A_iNi[Cr(CN)_6]_j \cdot nH_2O$ (NiCr), have raised the temperature of photocontrol to 70 K, in addition to reversing the sign of the effect [2,3]. This photodecrease in magnetization has been posited to arise from strain-induced spin canting in the NiCr layer, similar to pressure effects in a comparable single-phase material [4]. Ongoing studies seek to verify and quantify this model with a series of CoFe-NiCr core-shell particles of varying shell thicknesses.

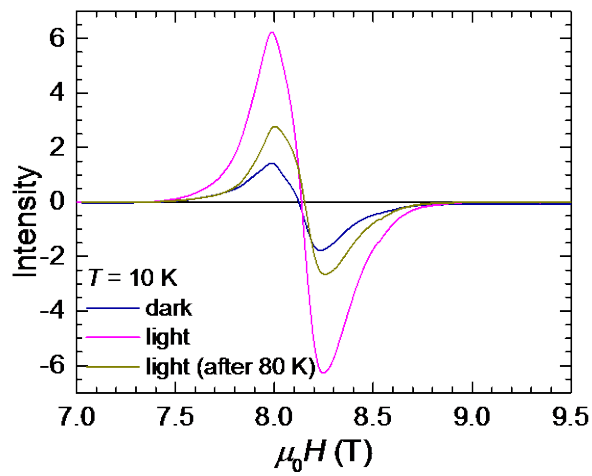

Figure 1. Transmission EPR (f ~ 240 GHz) at 10 K before (dark) and after (light) ~14 hrs of white light irradiation, and after warming to 80 K.

Experimental Details

Transmission EPR (f = 239 GHz) was performed on a powder sample suspended in vacuum grease. At 300 K and 5 K, the field was swept over the full range (0 – 12 T) to search for signal. After slowly cooling from 300 K, spectra (7.0 T – 9.5 T) were acquired from 5 K to 80 K. For the light state measurements, the sample was irradiated with white light, and after irradiation, the temperature-dependent spectra were again acquired.

Results and Discussion

Within the parameter space studied, only one signal was observed near 8 T. After overnight irradiation at 10 K, a significant increase in the magnitude of the signal was observed, consistent with a photoincrease in the number of spins in the CoFe constituent, **Figure 1**. However, after warming to 80 K, a large decrease in the signal was seen, though it did not return completely to the dark state magnitude. Irradiation at 40 K appeared to have no effect, but after subsequent thermal cycling down to 5 K and back to 40 K, a decrease in the signal was observed, **Figure 2**.

Summary

Significant photoeffects were observed in the EPR signal of CoFe-NiCr core-shell particles. The initial effects are consistent with PPIM in pure CoFe. The subsequent decreases in signal, however, point to a model that incorporates a decrease of spins in the NiCr, in addition, or as an alternative explanation, to any spin canting.

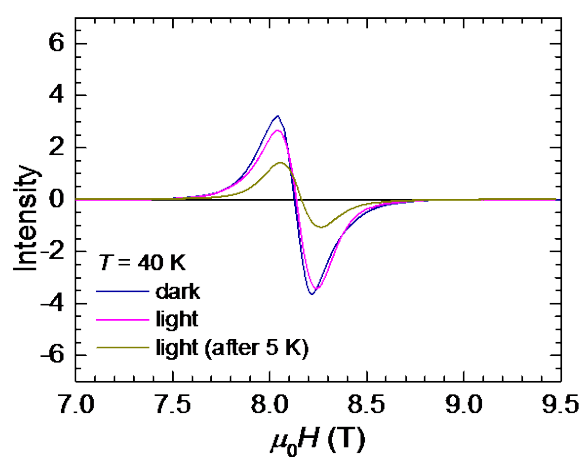

Figure 2. Transmission EPR (f ~ 240 GHz) at 40 K before (dark) and after (light) ~14 hrs of white light irradiation, and after cooling to 5 K.

Acknowledgements

This work was supported, in part, by the NSF through DMR-1202033 (MWM), DMR-1005581 (DRT), and DMR-0654118 (NHMFL).

References

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