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Effect of pressure on the magnetic properties of LiCuFe and LiCuFe@LiNiCr Prussian blue analogues

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ABSTRACT

Magnetic studies on the Prussian blue analogues (PBAs) $\text{Li}_x \text{Cu}_y [\text{Fe}(\text{CN})_6]_z \cdot m\text{H}_2\text{O}$ (LiCuFe–PBA) and $\text{Li}_j \text{Ni}_k [\text{Cr}(\text{CN})_6]_t \cdot n\text{H}_2\text{O}$ (LiNiCr–PBA), as well as LiCuFe@LiNiCr–PBA core–shell heterostructures, have been conducted under pressures ranging from ambient to ≈ 1.4 GPa and at temperatures of 2–90 K. The results for the single component CuFe–PBA indicate robust magnetic properties under the range of pressures studied where a $T_c = 20$ K was observed at all pressures. Our pressure studies of single component NiCr–PBA are consistent with previously published results by other workers below 1.0 GPa. However, at pressures above 1.0 GPa, the decrease in magnetization is accompanied by a decrease in the T_c , an indication of changes in the superexchange value. The results obtained with the single component samples can be mapped onto the observations of the heterostructures.

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1. Introduction

Prussian blue analogues (PBAs) are an interesting class of molecular magnets because their properties may be tuned chemically and by external stimuli [1]. In general, PBAs are face-centered cubic (fcc) systems with the molecular formula $A_i M_i [M'(CN)_6]_k \cdot m H_2 O (MM' -$ PBA) where *M* and *M*' are transition metal ions, A is an alkali ion, and *i*, *j*, *k*, and *m* are rational numbers. Their magnetic properties arise from the superexchange mediated by the cyanide (CN) bridge between the transition metal centers ($M'-C \equiv N-M$). The superexchange interaction is responsible for the magnetic ordering characterised by transition temperatures (T_c) ranging from 5.6 K for Fe^{III}[Fe^{II}(CN)₆]_{3/4}·3.7 H₂O to 376 K for KV^{II}[Cr^{III}(CN)₆][1]. In addition, the superexchange interaction is determined by the symmetry and the energy of the magnetic orbitals of the constituent metal ions according to Anderson and Goodenough-Kanamori rules [2-5]. Some properties of PBAs include persistent photoinduced magnetism (PPIM) [6,7], charge transfer induced spin transition (CTIST) [8], and pressure induced electron transfer (PIET) [9].

Recent developments have employed thin films [10,11] and nanoparticles [12] of heterostructured PBAs to enhance the overall properties of the individual constituents. Specifically, the photocontrol temperature has been increased from 20 K (the T_c for the single-component CoFe–PBA) to 70 K (the T_c of the NiCr–PBA constituent) [10] and similar results are present in analogous core–shell nanoparticles [12].

In the current study, pressure is used to probe PBAs in an effort to understand the relationship between structural changes and magnetic properties. Prussian blue analogues such as CoFe-PBA and NiCr-PBA have been shown to be sensitive to pressure whereby application of pressure leads to a decrease in the magnetization [9,13]. In particular under pressure, CoFe-PBA undergoes a pressure induced electron transfer (PIET) which switches the high spin Fe^{III} (S = 1/2)-CN-Co^{II} (S = 3/2) to low spin Fe^{II} (S = 0)-CN-Co^{III} (S = 0). The PIET is accompanied by a change in the transition temperature due to changes in the superexchange interaction [9]. On the other hand, NiCr–PBA, a ferromagnet (T_c = 70 K) does not exhibit any change in transition temperatures up to $P \approx 0.9$ GPa, but a reduction in magnetization has been attributed to the canting of the spins of the metal ions [13]. However, pressure studies on MnCr-PBA, a ferrimagnet, showed an increase in the transition temperature with pressure, from $T_c \approx 65$ K at ambient to 90 K at 0.86 GPa with a $\Delta T_c / \Delta P = 25.5$ K GPa⁻¹ [13].

The present work centers on the LiCuFe@LiNiCr-PBA heterostructures (employing the core@shell notation), focusing on results obtained from the individual components and comparing our results with observations on the heterostructures by primarily considering the interplay between magnetism and pressure.

2. Experimental methods

2.1. Materials

 $K_3Cr(CN)_6$ was synthesized by treating aqueous solutions of potassium cyanide with $CrCl_3 \cdot 6H_2O$ and used after recrystallization from methanol [14]. Deionized water used in synthetic procedures



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was obtained from Barnstead NANOpure system. All of the other reagents were purchased from Sigma–Aldrich, Fisher Scientific, or Acros Organics and used without further purification. Fast PES Bottle Top Filters with 0.45 μ m pore size (Nalgene) were used during the synthesis.

2.2. Core particles (LiCuFe)

A 400 mL aqueous solution of CuCl₂·2H₂O (0.272 g, 1.60 mmol) and LiCl (0.136 g, 3.21 mmol), and an equal volume of an aqueous solution containing K₃Fe(CN)₆ (0.508 g, 1.54 mmol) were simultaneously added dropwise to 700 mL of deionized water at room temperature. The solution was kept under vigorous stirring for approximately 24 h after complete addition. The particles were subsequently filtered under vacuum using a 0.45 µm filter before being washed with nanopure water, and resuspended by sonication for at least three cycles. The nanoparticles were then redispersed in 100 mL of nanopure water for use in the next step. After the biggest particles (>300 nm) were removed by centrifugation, the particles were redispersed in a 50:50 solvent mixture of water and acetone and air-dried yielding a powder.

2.3. Characterization results of LiCuFe

Li_{0.3}Cu₄[Fe(CN)₆]_{2.8}·7.5H₂O. Yellow powder. IR (KBr): 2103 cm⁻¹ (s, v_{CN} , Cu^{II}–NC–Fe^{III}); 2154 cm⁻¹ (w, v_{CN} , Cu^{II}–NC–Fe^{III}). EDS (Cu/Fe) 59.19:40.81.Yield: 197 mg (50%).

2.4. Core@shell particles (LiCuFe@LiNiCr)

The previously prepared core particles were redispersed in 600 mL of deionized water. A 400 mL aqueous solution of NiCl₂·6H₂O (0.180 g, 0.757 mmol) and LiCl (0.064 g, 1.51 mmol) and an equal volume of an aqueous solution of $K_3Cr(CN)_6$ (0.224 g, 0.688 mmol) were added using a peristaltic pump at a rate of 10 mL/h. The particles were filtered using a 0.45 µm filter, washed with nanopure water, and redispersed in 100 mL of nanopure water. Finally, the particles were redispersed in a 50:50 solvent mixture of water and acetone, air-dried, and isolated.

2.5. Characterization results of LiCuFe@LiNiCr

 $\begin{array}{ll} Li_{0.3}Cu_4[Fe(CN)_6]_{2.8}\cdot7.5H_2O@Li_{1.3}Ni_4[Cr(CN)_6]_{3.1}\cdot5.4H_2O. \ Lightbrown powder. IR (KBr): 2174 cm^{-1} (w, v_{CN}, Ni^{II}-NC-Cr^{III}); 2103 cm^{-1} (s, v_{CN}, Cu^{II}-NC-Fe^{III}); 2154 cm^{-1} (w, v_{CN}, Cu^{II}-NC-Fe^{III}). EDS (Cu/Fe) 31.70:21.86; (Ni/Cr) 26.18:20.26. Yield: 370 mg (92%). \end{array}$

2.6. Instrumentation

Infrared spectra were recorded on a Nicolet 6700 Thermo Scientific Spectrophotometer. Typically 16 scans were taken between 2300 and 1900 cm^{-1} with a resolution of 0.482 cm^{-1} . Powder samples were mixed with KBr and pressed into a pellet using 27.58 MPa. Transmission electron microscopy (TEM) was performed on a JEOL-2010 F HRTEM at 200 kV at the University of Florida Major Analytical Instrumentation Center. The TEM grids (ultrathin carbon film on holey carbon support film, 300 mesh, gold from Ted-Pella, Inc.) were prepared by dropping 40 µL of a solution containing 5 mg of sample dispersed by sonication in 1 mL of water for 30 min. Energy dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments EDS X-ray Microanalysis System coupled to the HRTEM microscope. A total of three scans were performed on different parts of the sample and then averaged to give relative atomic percentages for copper, iron, nickel, and chromium. Also, EDS linescans were performed on copper, iron, nickel, and chromium in order to see the core-shell heterostructure of the particles. Chemical formulas are based on metal composition from EDS, with water and counter cation (lithium) content determined from the number of trivalent metal vacancies ensuring electroneutrality.

2.7. Magnetic and pressure measurements

Magnetic measurements were performed using a "home-made" pressure cell designed for the commercial Quantum Design MPMS-XL7 SQUID magnetometer. The pressure cell is made entirely of beryllium copper (BERYLCO-25), except the sample holder, which is made of teflon, with an OD of 2.39 mm and an ID of 1.65 mm. The beryllium copper parts include a cell body in the shape of a pressure cylinder with outer and inner radii (the sample space) of 8.38 and 2.39 mm, respectively. Pressurization is achieved by the use of two screws that cap the ends of the cell body. The cylindrical geometry of the cell ensures a uniform symmetry, thereby minimizing the background contribution from the beryllium copper.

The sample, typically with a mass of ~5 mg is loaded into the sample can with a piece of superconducting lead (Pb) as the manometer. To achieve isotropic pressure, a pressure transmitting fluid, Daphne 7373, is added to the sample. This oil has been shown to have minimal relaxation (≈ 0.2 GPa) when cooled from room temperature to 2 K [15,16]. The pressure inside the cell is determined using the pressure-dependent superconducting transition of lead. The relationship between the T_c and pressure is known to be linear and given by $\Delta T/\Delta P = 0.405$ K/GPa [17]. The maximum pressure for this pressure cell is approximately 1.4 GPa. All pressures were applied at room temperature. Samples were then cooled to 5 K, and all data were taken while warming in a field of 100 G.

3. Results

The HRTEM images of the core and core-shell particles are shown in Fig. 1. The LiCuFe-PBA core appears darker in comparison to the LiNiCr shell. The particle size distribution was measured from the TEM images using ImageJ software [18]. A histogram (see Supporting information) of the particle sizes showed particle growth from the synthesis of the core to the full core@shell configuration. Furthermore, the EDS linescans confirmed the chemical composition of each layer of the core-shell particles (see Supporting information). In addition, room temperature Fourier transform infrared (FT-IR) spectra shows a peak at 2103 cm⁻¹, corresponding to the of Cu^{II}-NC-Fe^{III} cyanide stretching bands of the cores. An additional peak observed at 2174 cm⁻¹ corresponds to the Ni^{II}-NC-Cr^{III} stretch of the shell (see Supporting information).

In the case of the single component LiCuFe–PBA, temperature sweeps from 5 to 40 K showed no significant changes in the magnetization at different pressures (Fig. 2). In addition, the transition



Fig. 1. HRTEM images of (a) LiCuFe-PBA core particles and (b) a single LiCuFe@LiNiCr-PBA core@shell particle.

temperature of the LiCuFe–PBA was measured to be 20 K, which is consistent with published values [1,19]. Our results show no significant changes in the transition temperature at all pressures (ambient, 0.42, and 1.26 GPa), implying a robust superexchange pathway between the Cu^{II}–NC–Fe^{III} metal centers.

The magnetic response of the core@shell particles under pressure was measured at ambient, 0.42, 1.08, and 1.36 GPa, as shown in Fig. 3 (see Supporting information for 3D plot). Two transition temperatures were observed at $T_c^{\text{low}} \approx 20$ K and $T_c^{\text{high}} \approx 70$ K. The low transition temperature at 20 K remains constant at all pressures and is consistent with results obtained for the LiCuFe–PBA cores, Fig. 2. On the other hand, below 1.0 GPa, the T_c^{high} (P < 1.0 GPa) = 70 K, corresponding to the LiNiCr–PBA component, is independent of pressure, and these observations are consistent with those reported by Zentková et al. [13]. However, above 1.0 GPa, T_c^{high} reduced from 70.0 K ($P \leq 0.42$ GPa) to 68.0 K ($P \sim 1.08$ GPa) and 65.5 K ($P \sim 1.36$ GPa). In addition, it is also noteworthy that the increase in pressure was accompanied by a decrease in the overall magnetization.

Finally, to confirm that the changes in transition temperature and the reduction in magnetization observed in the core@shell particles are primarily due to the NiCr–PBA shell, single-component KNiCr–PBA was measured under similar conditions as those described previously. The magnetization versus temperature plot (Fig. 4), had similar features to the heterostructures between 50 and 90 K.

4. Discussion

The effect of pressure on the magnetism of PBAs can be understood qualitatively by considering the superexchange interaction between the metal centers, which can be either ferromagnetic or antiferromagnetic depending on the orbital symmetries and energies. The unpaired electrons of the metal centers can be found in the d-orbital. Thus, by ligand field theory, these electrons reside in the t_{2g} and/or e_g orbitals. Qualitatively, the superexchange value is directly proportional to $2S(\Delta^2 - \delta^2)^{1/2}$ where δ is the energy gap between umixed orbitals, Δ is the energy gap between orbitals built from them, and *S* is the monoelectronic overlap integral [1]. Therefore, any change in these parameters correlates with a change in the transition temperature. Typically, the application of pressure increases in the overlap integral through the reduction of the unit cell volume. For an antiferromagnetic coupling, the re-



Fig. 2. The magnetization of LiCuFe–PBA under pressure. The samples were cooled and measured in a field of 100 G at pressures of ambient (square), 0.46 GPa (circle) and 1.26 GPa (triangle). No significant change in magnetization was observed for all pressures.



Fig. 3. Magnetic data on core@shell PBA. (a) The magnetization as a function of temperature and (b) the derivative of the magnetization with respect to temperature as a function of temperature at different pressures. The plots depict features found in the individual components. The $T_c = 20$ K can be attributed to the LiCuFe-PBA core, and the $T_c = 70$ K is due to the LiNiCr-PBA shell, which changes at pressures greater than 1.0 GPa. A 3D plot of magnetization vs. temperature and pressure is shown in the Supporting information.

sult is an increase or decrease in the superexchange value and hence the Néel temperature, T_N . In the case of ferromagnetic coupling, the overlap integral *S* is zero; consequently, application of pressure leads to no significant changes in the transition temperature. Furthermore, pressure can affect the bonding angles between the magnetic centers and hence the overall cubic symmetry of the unit cell. The manifestation of such an effect may be an increase or decrease in the magnetization and/or changes in the transition temperature.

The magnetic coupling of the PBAs in this study (CuFe-PBA and NiCr-PBA) have been shown to be ferromagnetic [1,13,19]. Consequently, their magnetic response to the application of pressure should not be significant. Our observation of the effect of pressure on LiCuFe-PBA is consistent with the above hypothesis, whereby no changes in the magnetization nor the transition temperatures were measured up to \approx 1.4 GPa. On the other hand, our results on the LiNiCr-PBA agree with the above hypothesis only up to 1.0 GPa. Above 1.0 GPa, the transition temperature shifts to lower temperatures, and this behaviour may be attributed to a reduction in the magnetic coupling, caused by a structural change in the system. It is noteworthy that linkage isomerism has been reported in a similar analogue, CsNiCr-PBA [1], where the high spin nickel atoms are reduced to low spin. The manifestation of this effect can be observed as decrease in magnetization and/or a reduction in the transition temperature. Therefore our observations of the LiNiCr-PBA



Fig. 4. Plots of (a) magnetization, *M*, as a function of temperature, *T* (see Supporting information for 3D plot). (b) The derivative of magnetization as a function of temprature of KNiCr-PBA. A decrease in magnetization is observed with increasing pressure. In addition, above 1.0 GPa, the transition temperature decreases. Measurements were performed in a field of 100 G.

system may also be due to linkage isomerism induced by the application of pressure but our current magnetic data is insufficient to support this claim. Further analysis from infrared and Raman spectra showing the effect of pressure on the cyanide stretching bands will be needed to confirm the presence or absence of pressure induced linkage isomerism. The results from the core@shells can be mapped onto and explained by observations in our single component measurements, that is, the reduction in magnetization observed is a result of external stress on the LiNiCr-PBA shells.

5. Conclusion

The effect of pressure on LiCuFe@LiNiCr-PBA has been studied up to \approx 1.4 GPa. Our results show two transition temperatures at 20 and 70 K, attributed to the LiCuFe-PBA and the LiNiCr-PBA, respectively, and a pressure-induced decrease in magnetization. At all pressures, our results showed no changes in the magnetic ordering at 20 K. On the other hand, above 1.0 GPa, the transition temperature at 70 K shifts to lower temperatures. The observation for the single component LiCuFe-PBA indicates robust magnetic properties for pressures ≤1.4 GPa whereby no change in the superexchange value was observed. However, the pressure studies of single component NiCr-PBA are consistent with observations by Zentková et al. [13] up to 1.0 GPa. Below 1.0 GPa, our data show a reduction in magnetization that might be attributed to the canting of the spins at the molecular level but no change in the ferromagnetic ordering temperature ($T_c \approx 70$ K). At pressures above 1.0 GPa, the decrease in magnetization is accompanied by a decrease in the T_c , an indication of changes to the superexchange value. It is noteworthy that the pressure independent magnetization of the single component LiCuFe-PBA is preserved when incorporated into the LiCuFe@LiNiCr core-shell.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.05.011.

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