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Electronic phase separation and magnetic-field-induced emergent phenomena in molecular multiferroic $(ND_4)_2FeCl_5{\cdot}D_2O$

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Electronic phase separation has been increasingly recognized as an important phenomenon in understanding many of the intriguing properties displayed in transition metal oxides. It is believed to produce fascinating functional properties in otherwise chemically homogenous electronic systems, e.g. colossal magnetoresistance manganites and high-T_c cuprates. While many well-known electronically phase separated systems are oxides, it has been argued that the same phenomenon should occur in other electronic systems with strong competing interactions. Here we report the observation of electronic phase separation in molecular $(ND_4)_2FeCl_5{\cdot}D_2O$, a type-II multiferroic. We show that two magnetic phases, one of which is commensurate and the other of which is incommensurate, coexist in this material. Their evolution under applied magnetic field produces emergent properties. In particular, our measurements reveal a field-induced exotic state linked to a direct transition from a paraelectric/paramagnetic phase to a ferroelectric/antiferromagnetic phase, a collective phenomenon that hasn't been seen in other magnetic multiferroics.

There is mounting evidence that electronic phase separation is an intrinsic property of strongly correlated electron materials[1–4]. The intricate interplay between spin, charge, orbital, and lattice degrees of freedom often results in "electronically soft" phases of matter with inhomogeneous and mixed order in correlated materials leading to emergent properties[3]. Electronic phase separation has been shown to have profound effect on the macroscopic properties of a wide range of materials including cuprates[5], iron pnictides[6,7], colossal magnetoresistance manganites[3,8–11], and ferrites[12,13]. Recent work further demonstrates that the competing phases in electronically phase separated materials can be tuned and controlled by spatial confinement[10,11], providing insights on how to manipulate the collective phenomena. It is of great interest to explore the exotic behaviours arising from electronic softness in a large number of materials, particularly in systems which allow direct comparison between theory and experiments for a deeper understanding of their origin. Here we report electronic phase separation in $(ND_4)_2FeCl_5{\cdot}D_2O$[14], a molecular system that exhibits magnetically-induced ferroelectricity[15]. Our results show that two magnetic phases, one commensurate and the other one incommensurate, coexist in this material. Moreover, their competition gives rise to fascinating phenomena under the influence of magnetic field.

$(ND_4)_2FeCl_5{\cdot}D_2O$ is a type-II multiferroic[16,17] that exhibits intriguing magnetic and ferroelectric properties[15,18–20]. At zero magnetic field, this system undergoes two successive magnetic transitions upon cooling at T_N=7.3 K and T_{FE}=6.8 K, with the latter accompanied by spontaneous ferroelectric polarization. The magnetic structure changes from a collinear sinusoidal between $T_{FE}<T<T_N$ to a cycloidal spiral below T_{FE}=6.8 K[18] characteristic of a type-II multiferroic with inverse DzyaloshinskyMoriya interactions. A very rich magnetic field versus temperature (H vs. T) phase diagram is obtained when applying a magnetic field parallel to either the a or c-axis. As shown in Ref. 15 for $H\|a$, a modest magnetic field induces transitions to distinct magnetic and ferroelectric phases. They are labeled as ferroelectric I (FE I), ferroelectric II (FE II), and ferroelectric III (FE III), respectively[15]. The magnetic structure associated with the FE I phase is an incommensurate cycloidal (ICC, with a characteristic wave vector k_1=(0 0 k_{z1}), $k_{z1} \approx 0.23$ at 1.5 K). The magnetic structures corresponding to FE II and FE III phases are a distorted cycloid (C1) and a quasi-collinear structure (C2), described by commensurate wave vectors k_2=(0 0 k_{z2}) (k_{z2}=0.25) and k_3=(0 0 0)[20]. The transition from FE I to FE II at 2.8 T has been described as an incommensurate-to-commensurate lock-in transition, and the transition from FE II to FE III at 5 T has been identified as a spin-flop transition[20]. The electric polarization $P1$ associated with the FE I phase is only slightly different from $P2$ of phase FE II. Both $P1$ and $P2$ lie in the ab-plane and slightly tilt away from the a-axis, with $\sphericalangle(P1, a) \simeq 7°$ in FE I and $\sphericalangle(P2, a) \simeq 9°$ in FE II, indicating that these soft phases are very close in energy. The electric polarization in phase FE III is very different: it points along the c-axis and is accompanied by a spin-flop transition.

We note that this intriguing phase diagram contains features that are not fully understood. For example, as pointed out in Ref. 20, the incommemsurate-to-commensurate magnetic transition (with changes in the

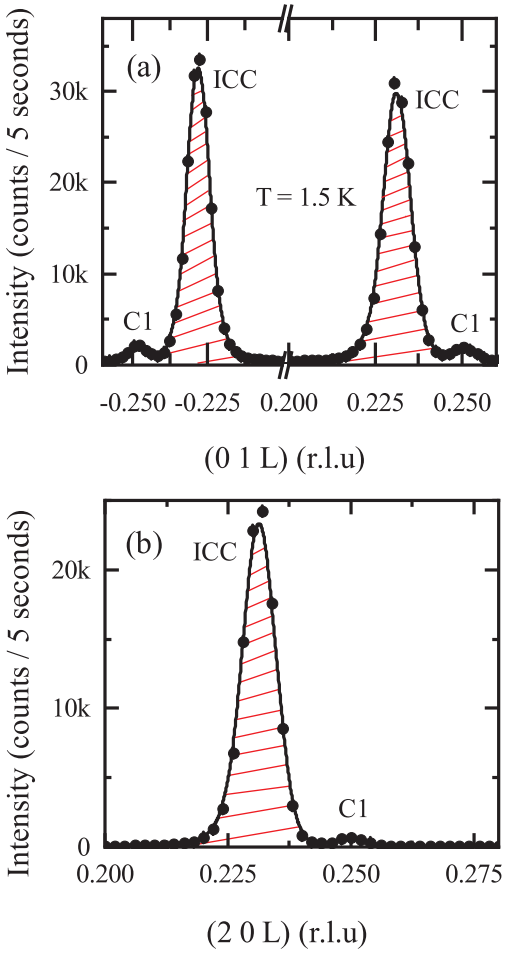

FIG. 1. (Color online) L-scans along (a) (0 1 L) and (b) (2 0 L)-directions illustrate the coexistence of incommensurate (ICC, wave vector k_1=(0 0 k_{z1}), $k_{z1} \approx 0.23$) and commensurate (C1, wave vector k_2=(0 0 k_{z2}), $k_{z2} \approx 0.25$) phases at 1.5 K and 0 T.

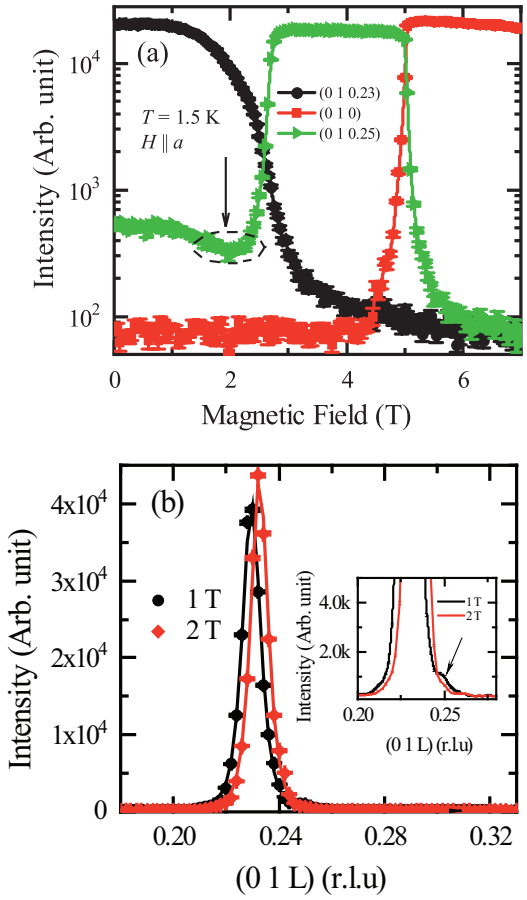

FIG. 2. (Color online) Neutron diffraction data measured with $H \| a$ at 1.5 K. (a) Neutron diffraction intensity as a function of magnetic field obtained by counting at the peak position of (0 1 0.23), (0 1 0.25), and (0 1 0) magnetic peaks. The (0 1 0.23), (0 1 0.25), and (0 1 0) peaks are associated with the incommensurate ICC, commensurate C1 and C2 states as described in the text. The black arrow and the ellipse in dashed line indicate an anomalous dip between 1.5 T and 2.5 T in the data of the (0 1 0.25) peak. (b) L-scans along (0 1 L) measured at $\mu_0 H$ = 1, and 2 T. The inset depicts the disappearance of the weak (0 1 0.25) peak at 2 T.

magnetic wave vector from (0 0 ≈0.23) to (0 0 0.25)) associated with the purported lock-in transition at 2.8 T cannot be explained from the small changes in the a-axis due to magnetostriction[15]. Moreover, the direct transition from a paraelectric/paramagnetic (PE/PM) phase to a ferroelectric/antiferromagnetic (FE/AFM) phase observed in a narrow range between 2 and 3 T is rather rare. As in most cases this transition occurs via an intermediate paraelectric, antiferromagnetic state[21]. It has been suggested that such a direct transition would require two simultaneous order parameters[21–23]. In this Letter, we show that both features can be fully accounted for by the coexistence of soft phases, with incommensurate (ICC) and commensurate (C1) orders, respectively.

In prior work, we reported that the magnetic ground state of $(ND_4)_2FeCl_5 \cdot D_2O$ is inhomogenous[19]. We observed odd and even higher-order harmonics associated with the incommensurate cycloid wave vector k_1 and a coexisting secondary magnetic phase described by the commensurate wave vector. As shown in Fig. 1, the (0 0 0.25)-type commensurate peak coexists with the primary (0 0 ≈0.23)-type incommensurate peak in multiple scans at various Q-positions. Polarized neutron diffraction measurements indicate that they are both magnetic in origin. Because their peak widths are comparable, the ICC and C1 phases have similar magnetic correlation lengths along the c-axis. These results provide concrete evidence that the ground state of $(ND_4)_2FeCl_5 \cdot D_2O$ is intrinsically inhomogenous with coexisting incommensurate and commensurate orders. Here, we illustrate the subtle effects resulting from the strong phase competition between ICC and C1 that shed light on the field-induced emergent phenomena in this material.

Figure 2(a) compares the field dependence of the (0 1 0.23), (0 1 0.25), and (0 1 0) magnetic peaks associated with three distinct magnetic structures: incommensurate

cycloidal (ICC) in FE I, distorted cycloid (C1) in FE II and quasi-collinear structure (C2) in FE III. At first glance two field-induced transitions are clearly observed at 2.8 T and 5 T in agreement with Ref. 20, in which the 2.8 T transition is attributed to an incommensurate-commensurate lock-in transition from ICC to C1 with the peak center of (0 1 0.23) gradually shifting towards (0 1 0.25). However, as we examine the data in more detail, an anomalous dip in the intensity of the (0 1 0.25) peak is observed around 1.5-2.5 T before the ≈2.8 T transition. This is totally unexpected as it is counter to the proposed incommensurate-commensurate lock-in transition. For a lock-in transition from ICC to C1, the peak position would gradually shift from (0 1 0.23) to (0 1 0.25) and the peak intensity of (0 1 0.23) would gradually decreases while the peak intensity of (0 1 0.25) would increase monotonically with increasing field. In order to understand the origin of the anomalous dip, we compare the L-scans measured along (0 1 L) at 1 T and 2 T (Fig. 2 (b)), which clearly shows that the weak (0 1 0.25) peak disappears at 2 T. The data suggests that (0 1 0.23) and (0 1 0.25) merge into a single peak at 2 T with enhanced peak intensity, indicating the anomalous dip that anticipates a transition is an intrinsic effect.

In order to reveal the subtle field-induced effects arising from phase competition between ICC and C1, we further compare L-scans measured along the (0 1 L)-direction at selected fields in Fig. 3. The coexistence of C1 and ICC is clearly observed at 1 T (Fig. 3 (a)), 2.6 T (Fig. 3 (c)) and 2.8 T (Fig. 3 (d)) with both (0 1 0.25) and (0 1 0.23) peaks present in the scan. As the mixture of C1 and ICC evolves under applied magnetic field, the total volume is conserved: the increase of the C1 volume is matched by a decrease of the ICC volume. This is unambiguously illustrated in Fig. 3 (c) and (d) by comparing the relative intensity between (0 1 0.23) and (0 1 0.25) at 2.6 T and 2.8 T. These results clarify the nature of the transition at 2.8 T. Compared to the relative volumes of ICC and C1 in the mixed state, the ICC phase is dominant at 2.6 T while C1 is dominant at 2.8 T. The transition is accompanied by modest magnetostriction[15], suggesting that the C1 phase is coupled more strongly with the lattice than the ICC phase. The ability to tune from ICC to C1 with a 2-3 T field indicates that these phases are electronically soft and sensitive to external perturbations, i.e. pressure, and magnetic field. As field is further increased, the ICC phase continues to shrink. The ICC phase is completely suppressed at 4 T (Fig. 3 (e)).

Other striking features observed at 2 T are the distinct single peak shape, and the disappearance of higher-order harmonic peaks (Fig. 3 (b)) in contrast with the scans measured at other fields. Higher-order harmonic peaks are clearly visible in the scans measured at 1 T, 2.6 T, and 2.8 T in the mixed state of ICC and C1 (the 5th-order harmonic peak is outside the plot range in Fig. 3 (a)). The absence of the higher-order harmonic peaks at 2 T suggests that the state between 1.5-2.5 T (corresponding to the anomalous dip in Fig. 2 (a)) is not a simple mix-

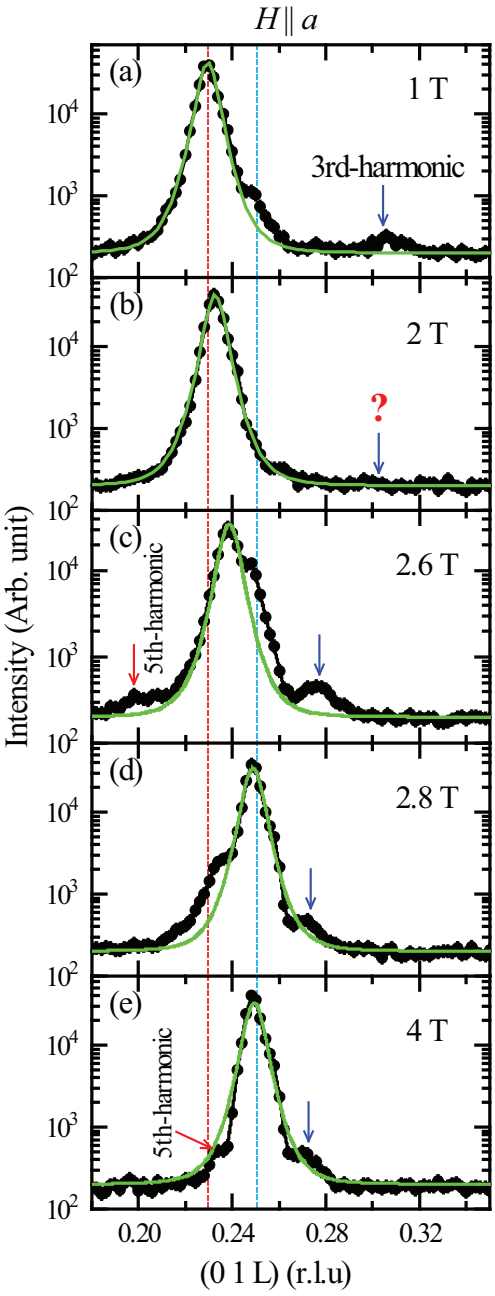

FIG. 3. (Color online) L-scans measured along (0 1 L) at selected fields, $T = 1.5$ K. (a) $\mu_0 H = 1$ T; (b) $\mu_0 H = 2$ T; (c) (a) $\mu_0 H = 2.6$ T; (d) (a) $\mu_0 H = 2.8$ T; (e) $\mu_0 H = 4$ T. The intensity is plotted in logarithmic scale. The blue and red arrows point to the 3^{rd}-order and 5th-order harmonic peaks associated with the incommensurate phase. The dotted red and cyan lines depict the peak centers associated with the ICC and C1 phases at (0 1 ∼0.23) and (0 1 ∼0.25), respectively. The solid green curves are fitting results to a Squared-Lorentzian function. The data measured at 2 T in (b) can be fitted to a single peak. For comparison, the data at 1 T, 2.6 T, 2.8 T and 4 T are also fitted to a single peak, with fixed constant background and peak width using the same values obtained from the fitting to the 2 T data.

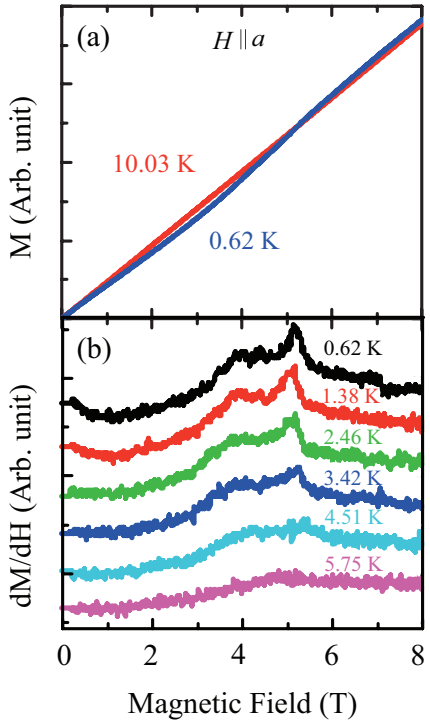

FIG. 4. (Color online) Magnetization (a) and the first derivative of the magnetization (b) measured with $H\|a$. Two peaks are observed in $\mathrm{d}M/\mathrm{d}H$ corresponding to the complete suppression of the ICC phase and the spin flop transition.

ture of ICC and C1 but is rather an exotic field-induced state. Our data suggests that this exotic phase may be described as a bicritical-state emerging from the interplay between ICC and C1. It is no coincidence that this exotic state seems to be closely related to the unusual region in the H vs. T phase diagram where a direct transition from a PE/PM state to a FE/AFM state was reported in Ref. 15. The direct transition is also supported by our neutron diffraction measurements[14]. It has been proposed that such behavior requires two different order parameters[21–23]. The coexistence of ICC and C1 orders suggests that this hypothesis is realized in $(ND_4)_2FeCl_5\cdot(D_2O)$[24].

These findings are also supported by magnetization results. Figure 4 displays magnetization with field applied along the a-axis. Below T_N=7.3 K, a distinct step is observed in the magnetization at 5 T, which has been attributed to spin flop transition[15,20]. This type of anisotropy-driven spin reorientation is typically first order[25–27], although there are exceptions[28]. In $(ND_4)_2FeCl_5\cdot(D_2O)$, the spins are mainly confined in the ac-plane with no easy axes[15,20]. The spin flop transition is accompanied by lattice changes indicating that the transition is mediated by spin-lattice coupling. Careful examination of the $(\mathrm{d}M/\mathrm{d}H)_T$ curves, however, uncovers different and more complex behavior. The derivative curves in Fig. 4 (b) reveal an additional anomaly at 4 T besides the spin flop transition at 5 T. The step-wise character of this curve is most evident at 0.62 K. It persists to higher temperature and disappears entirely above 4.5 K. This anomaly coincides with the complete suppression of the ICC phase at 4 T from neutron measurements. More interestingly, the transition at 4 T is also linked to a change in electric polarization from $P1$ to $P2$. The electric polarization is slight reoriented towards b-axis, with $\sphericalangle(P1,a)\simeq 7^\circ$ for $\mu_0 H$ <4 T to $\sphericalangle(P2,a)\simeq 9^\circ$ for $\mu_0 H$>4 T[15].

To summarize, we performed neutron scattering and magnetization measurements to study the magnetic properties of $(ND_4)_2FeCl_5\cdot(D_2O)$. We show direct evidence that the incommensurate ICC and commensurate C1 phases – associated with two different ferroelectric states – coexist in this frustrated magnet[29], and that their interplay under applied magnetic field produces emergent properties. The subtle field-induced effects presented here provide insights into the emergent phenomena in $(ND_4)_2FeCl_5\cdot(D_2O)$. Our results indicate the transition at 2.8 T is not a simple incommensurate-commensurate lock-in transition but rather reflects the tuning of two electronically-soft phases by the magnetic field with the ICC phase dominant below 2.6 T and the C1 state dominant above 2.8 T. In particular, our measurements reveal an exotic state linked to a direct transition from a PE/PM state to an FE/AFM state in the H vs. T phase diagram for $H\|a$. Our data indicates that this exotic state is not a simple mixture but rather an entangled, bicritical-state phase of ICC and C1. This observation is reminiscent of the lattice strain effect observed in $La_{0.5}Ca_{0.5}MnO_3$ between T_C and T_N that was attributed to the simultaneous presence in different domains of several metastable states[30]. Indeed, the observation of even-order harmonics associated with incommensurate wave vector[19], the magnetostriction and negative thermal expansion[15] all indicate that spin-lattice coupling plays a key role in coupling the magnetic and ferroelectric properties in $(ND_4)_2FeCl_5\cdot(D_2O)$. Due to its "softness", $(ND_4)_2FeCl_5\cdot D_2O$ can serve as a test bed for theoretical modeling. To our knowledge, this is the first time that the coexistence of competing magnetic phases has been observed in a non-oxide type-II multiferroic system. The results presented here will initiate further investigations to uncover the fundamental nature of this collective phenomenon.

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[1] E. Dagotto, Complexity in strongly correlated electronic systems. Science **309**, 257-262 (2005).
[2] A. Moreo, S. Yunoki, E. Dagotto, Phase separation scenario for manganese oxides and related materials. *Science*, **283(5410)**:2034 (1999).
[3] G. C. Milward, M. J. Calderón, and P. B. Littlewood, Electronically soft phases in manganites. *Nature* **433**, 607-6010 (2005).
[4] A. Zorko, O. Adamopoulos, M. Komelj, D. Arcon, and A. Lappas, Frustration-induced nanometre-scale inhomogeneity in a triangular antiferromagnet. *Nature Communications*, **5**,3222 (2014).
[5] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Evidence for stripe correlations of spins and holes in copper oxide superconductors. *Nature* **375**, 561-563 (1995).
[6] J. T. Park, D. S. Inosov, Ch. Niedermayer, G. L. Sun, D. Haug, N. B. Christensen, R. Dinnebier, A. V. Boris, A. J. Drew, L. Schulz, T. Shapoval, U. Wolff, V. Neu, Xiaoping Yang, C. T. Lin, B. Keimer, and V. Hinkov, Electronic phase separation in the slightly underdoped iron Pnictide superconductor $Ba_{1-x}K_xFe_2As_2$. *Phys. Rev. Lett*, **102**, 117006 (2009).
[7] G. Lang, H.-J. Grafe, D. Paar, F. Hammerath, K. Manthey, G. Behr, J. Werner, and B. Buchner, Nanoscale electronic order in iron pnictides. *Phys. Rev. Lett.* **104**, 097001 (2010).
[8] E. Dagotto, T. Hotta, and A. Moreo, Colossal magnetoresistant materials: the key role of phase separation. *Phys. Rep.* **344**, 1-153 (2001).
[9] J. C. Loudon, N. D. Mathur, and P. A. Midgley, Charge-ordered ferromagnetic phase in $La_{0.5}Ca_{0.5}MnO_3$. *Nature* **420**, 797-800 (2002).
[10] Jian Shao, Hao Liu, Kai Zhang, Yang Yua, Weichao Yu, Hanxuan Lin, Jiebin Niu, Kai Du, Yunfang Kou, Wengang Wei, Fanli Lan, Yinyan Zhu, Wenbin Wang, Jiang Xiao, Lifeng Yin, E. W. Plummer and Jian Shen, Emerging single-phase state in small manganite nanodisks. *PNAS*, **113**, 9228-9231 (2016).
[11] Andreas Herklotz , Hangwen Guo , Anthony T. Wong , Ho Nyung Lee , Philip D. Rack , and Thomas Z. Ward, Multimodal responses of self-organized circuitry in electronically phase separated materials. *Adv. Electron. Mater.* **2**, 1600189 (2016).
[12] Jin Hong Lee,Kanghyun Chu, Ahmet A. Unal, Sergio Valencia, Florian Kronast, Stefan Kowarik, Jan Seidel, and Chan-Ho Yang, Phase separation and electrical switching between two isosymmetric multiferroic phases in tensile strained $BiFeO_3$ thin films *Phys. Rev. B* **89**, 140101(R) (2014).
[13] J. de Groot, K. Marty, M. D. Lumsden, A. D. Christianson, S. E. Nagler, S. Adiga, W. J. H. Borghols, K. Schmalzl, Z. Yamani, S. R. Bland, R. de Souza, U. Staub, W. Schweika, Y. Su, and M. Angst, Competing ferri- and antiferromagnetic phases in geometrically frustrated $LuFe_2O_4$. *Phys. Rev. Lett.* **108**, 037206 (2012).
[14] See Supplemental Material for experimental details and additional data.
[15] M Ackermann, D Bruning, T Lorenz, P Becker, and L Bohaty Thermodynamic properties of the new multiferroic material $(NH_4)_2[FeCl_5(H_2O)]$. *New Journal of Physics* **15**, 123001 (2013).
[16] S. W. Cheong, and M. Mostovoy, Multiferroics: a magnetic twist for ferroelectricity. *Nat. Mater (London)*, **6**, 13-20 (2007).
[17] D. Khomskii, Classifying multiferroics: Mechanisms and effects. *Physics* **2**, 20 (2009).
[18] J. A. Rodriguez-Velamazan, O. Fabelo, A. Millan, J. Campo, R. D. Johnson, and L. Chapon, Magnetically-induced ferroelectricity in the $(ND_4)_2[FeCl_5(D_2O)]$ molecular compound *Scientific Reports*, **5:14475**, DOI: 10.1038/srep14475.
[19] W. Tian, Huibo Cao, Jincheng Wang, Feng Ye, M. Matsuda, J.-Q. Yan, Yaohua Liu, V. O. Garlea, Harish K. Agrawal, B. C. Chakoumakos, B. C. Sales, Randy S. Fishman, and J. A. Fernandez-Baca, Spin-lattice coupling mediated multiferroicity in $(ND_4)_2FeCl_5{\cdot}D_2O$, *Phys. Rev. B* **94**, 214405 (2016).
[20] J. Alberto Rodriguez-Velamazan, Oscar Fabelo, Javier Campo, ngel Millan, Juan Rodriguez-Carvajal, and Laurent C. Chapon, Magnetic-field-induced change of magnetoelectric coupling in the hybrid multiferroic $(ND_4)_2FeCl_5{\cdot}D_2O$, *Phys. Rev. B* **95**, 174439 (2017).
[21] Pierre Toledano, Naemi Leo, Dmitry D. Khalyavin, Laurent C. Chapon, Tim Hoffmann, Dennis Meier, and Manfred Fiebig, Theory of high-temperature multiferroicity in cupric oxide. *Phys. Rev. Lett.* **106**, 257601 (2011).
[22] Gianluca Giovannetti, Sanjeev Kumar, Alessandro Stroppa, Jeroen van den Brink, Silvia Picozzi, and Jose Lorenzana, High-Tc Ferroelectricity Emerging from magnetic degeneracy in cupric oxide. *Phys. Rev. Lett.* **106**, 026401 (2011).
[23] Guangxi Jin, Kun Cao, Guang-Can Guo, and Lixin He, Origin of Ferroelectricity in high-Tc magnetic ferroelectric CuO. *Phys. Rev. Lett.* **108**, 187205 (2012).
[24] Note that the higher-order harmonic peaks are present at 4 T suggesting that the C1 phase may be incommensurate as well with a magnetic wave vector slightly different than (0 0 0.25).
[25] A. N. Bogdanov, A¿ V. Zhuravlev, and U. K. Rössler, Spin-flop transition in uniaxial antiferromagnets: Magnetic phases, reorientation effects, and multidomain states. *Phys. Rev. B* **75**, 094425 (2007).
[26] S. Foner and Y. Shapira, Magnetic phase transition in pure a Fe_2O_3. *Phys. Lett. A* **29**, 276 (1969).
[27] Y. Shapira, Ultrasonic behavior near the spin-flop transitions of hematite. *Phys. Rev.* **184**, 589 (1969)
[28] Michael O. Yokosuk, Sergey Artyukhin, Amal al-Wahish, Xueyun Wang, Junjie Yang, Zhiqiang Li, Sang-Wook Cheong, David Vanderbilt, and Janice L. Musfeldt, Track-

ing the continuous spin-flop transition in Ni_3TeO_6 by infrared spectroscopy. *Phys. Rev. B* **92**, 144305 (2015).

[29] Javier Campo, Javier Luzon, Fernando Palacio, Garry J. McIntyre, Angel Millan, and Andrew R. Wildes, Understanding magnetic interactions in the series $A_2FeX_5{\cdot}H_2O$ (A=K, Rb; X=Cl, Br). II. Inelastic neutron scattering and DFT studies. *Phys. Rev. B* **78**, 054415 (2008).

[30] P. G. Radaelli, D. E. Cox, M. Marezio, S -W. Cheong, P. E. Schiffer, and A. P. Ramirez, Simultaneous structural, magnetic, and electronic transitions in $La_{1-x}Ca_xMnO_3$ with x = 0.25 and 0.50. *Phys. Rev. Lett.* **75**, 4488 (1995).