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Change in Magnetic Properties upon Chemical Exfoliation of FeOCI

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S Supporting Information



ABSTRACT: The development of novel, intrinsic two-dimensional (2D) antiferromagnets presents the opportunity to vastly improve the efficiency of spintronic devices and sensors. The strong intrinsic antiferromagnetism and van der Waals layered structure exhibited by the bulk transition-metal oxychlorides provide a convenient system for the synthesis of such materials. In this work, we report the exfoliation of bulk FeOCl into and subsequent characterization of intrinsically antiferromagnetic thinlayer FeOCl nanosheets. The magnetic properties of bulk FeOCl, its lithium intercalate, and its nanosheet pellet are measured to determine the evolution of magnetic properties from the three-dimensional to the quasi-two-dimensional system. This work establishes FeOCl and isostructural compounds as a source for the development of two-dimensional intrinsic antiferromagnets.

INTRODUCTION

Recently, increased attention has been paid to the development of novel intrinsically magnetic nanosheets for spintronic applications and the production of novel heterostructure materials.¹⁻⁸ Candidate parent compounds for the production of such thin layers are typically magnetic materials which exhibit only weak interlayer attractive forces and thus are typically considerably easier to exfoliate into appreciably uniform nanosheets than nonlayered compounds.¹ Magnetic van der Waals (vdW) compounds are of particular interest, due to the wide range of magnetic, electronic, and physical properties exhibited by their bulk forms and the ease with which they may be delaminated into uniform nanostructures.² The recent development of liquid-based exfoliation methods has drawn significant attention for the ease by which such vdW compounds with very weak interlayer interactions may be uniformly delaminated into monolayer or few-layer sheets in large quantities.⁹ This represents a significant improvement over classical mechanical exfoliation with adhesive tape, which typically requires extended periods of tedious labor and often produces only small yields of fragile, non-single-layer nanosheets.^{10,11}

Recent developments in this field have focused largely on the production of novel magnetic 2D analogues of layered transition-metal trihalides, such as CrI₃,³ CrCl₃,⁵ RuCl₃,⁴ and VCl₃,⁶ as well as of layered dichalcogenides by use of mechanical exfoliation methods.¹² The chemical exfoliations of RuCl₃,⁴ $H_x CrS_2$,⁷ and MnO₂,⁸ some of the first two 2D magnetic systems produced in this manner, have established a baseline for the future production of less fragile 2D magnets.

In contrast to the transition-metal halide family of compounds, the transition-metal oxyhalide family of magnetic, layered vdW compounds has thus far received far less attention, despite the unusual magnetic properties exhibited by many of the bulk compounds.^{13,14} Three such compounds were recently predicted by Miao et al. to exhibit robust intrinsic ferromagnetic (CrOCl) and antiferromagnetic (VOCl, TiOCl) character in the two-dimensional monolayer.¹⁵ Here

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we study 2D FeOCl, the bulk of which has over time been extensively studied for various catalytic applications, as well for its potential use as a cathode material.^{16,17} Iron oxychloride and isostructural materials comprise the FeOCl structure type, which is defined by metal-oxygen double layers sandwiched between anionic layers, which are separated by van der Waals gaps.^{17,18} Beyond its potential in various catalytic systems, iron oxychloride has also been extensively studied for its magnetic properties. Bulk FeOCl has been characterized as an antiferromagnet that deviates from typical Curie-Weiss paramagnetic behavior.¹⁹ The observed susceptibility is nearly temperature independent, even slightly increasing, between 90 and 300 K. The observed room-temperature magnetic moment of bulk FeOCl has been reported by Kauzlarich et al. to be 2.76 $\mu_{\rm B}$, significantly lower than the 5.96 $\mu_{\rm B}$ expected for highspin Fe(III), which the authors attribute to strong antiferromagnetic Fe-Fe coupling, even above the Néel temperature $(\tilde{T}_{\rm N} = 90 \text{ K}).^{20}$

Over the years, a significant number of guest molecules have been intercalated into the interlayer space of FeOCl.^{20–23} Previous reports have shown that lithium-intercalated FeOCl typically shows a mixture of two distinct lithiated and nonlithiated regions, as well as a small but universal shift to lower angles in the pXRD diffraction pattern.^{17,24} The intercalation of various species into the FeOCl host structure is also reported to produce a uniform increase in magnetic susceptibility values.²⁴

Thin sheets of FeOCl have previously been synthesized and studied for their potential in catalytic applications.^{25–27} The first attempt at exfoliation of a sodium benzoate-intercalated FeOCl compound was reported in 2013, and the resulting nanosheets, for which no thickness or other properties were reported, were found to be composed of FeO⁺.²⁸ Since then, numerous groups have attempted to synthesize monolayer FeOCl nanosheets through a variety of methods, but the presented characterization using transmission electron microscopy (TEM) and atomic force microscopy (AFM) did not provide definitive proof for sample thickness below the fewlayer state.^{25–27,29,30} In addition, the magnetic properties of exfoliated FeOCl samples have not yet been studied, but the likelihood that exfoliated FeOCl will prove to be a source for a new 2D magnetic material warrants further investigation. Here, we report the exfoliation of FeOCl into uniform, very thin nanosheets. We study the magnetic properties of the exfoliated sheets by fabricating a pellet containing a few milligrams of the dried nanosheets. The nanosheet pellet, the magnetic properties of which differ from those of bulk FeOCl, also shows indications of frustrated magnetism. These results suggest that chemically exfoliated FeOCl nanosheets are a source for a novel 2D magnetic material.

RESULTS AND DISCUSSION

Bulk Synthesis and Characterization. Phase-pure bulk FeOCl powder was synthesized by a modified version of the thermal decomposition method reported by North et al.³¹ Unless they were stored under an inert gas atmosphere or in a desiccator, FeOCl samples were found to readily hydrolyze, eventually decomposing to hydrated FeCl₃. Lithium intercalation was achieved through a modified version of the *n*-butyllithium method.¹⁷ Further experimental details are given in the Supporting Information.

Figure 1 shows the powder X-ray diffraction (pXRD) data obtained for FeOCl powder, which is in agreement with the



Figure 1. pXRD patterns of synthesized FeOCl and Li_x FeOCl samples, in comparison to the simulated pXRD pattern for FeOCl.

simulated pattern for the bulk material; no impurity peaks are visible. The pXRD pattern of the synthesized Li_xFeOCl powder is shown to exhibit a small shift to lower angles, relative to FeOCl, for all major reflections, in agreement with previous studies (see enlarged view in Figure S1 in the Supporting Information).¹⁷ All reflections also exhibit broadening and a further reduction in intensity after lithiation. When lithiation conditions are particularly harsh (in terms of either increased reaction temperature or increased *n*-butyllithium concentration), there is a reduction in the intensity of the [010] reflection, and an additional reflection often appears in the pXRD pattern around $2\theta = 3.0^{\circ}$. This reflection corresponds to a *d* value of 13.6 Å, which relative to the *d* value of 7.90 Å for the [010] reflection suggests a pattern of FeOCl bilayers separated by lithium.

Analysis by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) of a representative FeOCl sample indicates the presence of a single-phase sample with a 1:1:1 Fe:O:Cl composition (see Figure S2). SEM/EDX analysis of a representative Li_xFeOCl sample indicates uniform elemental composition after lithium intercalation (Figure S3). Inductively coupled plasma mass spectrometry measurements performed on a representative Li_xFeOCl show a roughly 1:1:1:1 Li:Fe:O:Cl elemental composition.

Nanosheet Characterization. Liquid exfoliation of Li_x FeOCl was achieved through the addition of the sample powder to dry MeOH in a 1 mg to 2 mL ratio under argon flow and subsequent shaking for several days. For details, please see the Supporting Information.

TEM and EDX analysis of representative Li_xFeOCl samples exfoliated under low (~20%) relative humidity indicate the presence of very thin, well-defined FeOCl nanosheets, shown in Figure 2a. The uniform elemental composition of the exfoliated nanosheets is seen in Figure 3 and shows no region of clear Cl deficiency, indicating that they are still composed of Fe, O, and Cl after exfoliation. A well-defined diffraction pattern could be obtained for the FeOCl nanosheets (Figure 2b), indicating that the orthorhombic symmetry is retained. The observed intensity differences between the experimental and simulated [101] and [101] peaks are likely due to the



Figure 2. (a) TEM imaging of representative stacked FeOCl nanosheets. (b) Selected area electron diffraction pattern of a representative FeOCl nanosheet along the [010] zone axis. (c) Simulation of bulk FeOCl based on the space group *Pmmn* referenced in the literature.



Figure 3. (a) TEM imaging and (b) Fe, (c) O, and (d) Cl EDX elemental analysis of representative FeOCl nanosheets.

experimental diffraction pattern being taken on a thicker slab of stacked nanosheets (as seen in Figure 2a), which were slightly offset from each other. The experimentally derived *d* values are found to be consistent within 0.12 Å of the predicted values (Figure S4). Over a period of several days, the nanosheet suspension was observed to change color, where the initial black Li_xFeOCl suspension gradually turned purplebrown and eventually became brown-red after a period of more than 4 days in suspension. TEM/EDX analysis of Li_xFeOCl samples in suspension for a period of more than 6 days provided no evidence for the existence of FeOCl nanosheets, instead indicating only the presence of amorphous iron oxide particles. AFM characterization of representative Li_xFeOCl samples exfoliated under low (~20%) relative humidity shows relatively thin-layer nanosheets, roughly 0.5–1.0 μ m across (Figure S5). Due to slightly uneven substrate height, a definite nanosheet thickness could not be reliably determined, but topography profiles obtained suggest a thickness on the order of 2.0–2.4 nm, in comparison to the expected thickness of a true FeOCl monolayer, 0.79 nm. While the larger than expected thickness could be due to residual methanol coating of an FeOCl monolayer, it is more likely that the exfoliated nanosheets are bilayers, possibly with a small contribution from residual methanol.⁴ Samples of the nanosheet suspension drop-casted



Figure 4. Temperature-dependent ZFC (blue) and FC (orange) magnetic susceptibility and (insets) magnetization at 2 K (red) and at 300 K (green) of (a) FeOCl, (b) Li_x FeOCl, and (c) an FeOCl nanosheet pellet in an applied field of H = 10000 Oe.

onto a silicon wafer in moist air were observed to decompose within a period of a few minutes.

AFM characterization of representative Li_xFeOCl samples exfoliated under higher (~90–100%) relative humidity shows thicker, likely decomposed nanoparticles (Figure S6). The exfoliated sample is seen to consist of a relatively flat but fragmented surface on the order of 5.0 nm thick, with numerous holes, indicating decomposition. As bulk FeOCl is known to be extremely moisture sensitive, exposure to high humidity is likely to cause the decomposition and agglomeration of FeOCl nanosheets, contributing to the increased thickness and reduced uniformity of the sample surface observed.

Inert-atmosphere thermogravimetric analysis (TGA) characterization of a representative FeOCl nanosheet pellet, produced by the centrifugation and subsequent compaction of the nanosheet suspension, suggests that the nanosheets are relatively stable up to at least 523 K, albeit with a much lower crystallinity than in the original sample (see Figure S7b). Through fast heating to 523 K, the nanosheet pellet sample experienced a 9% mass loss, likely due to the evaporation of residual methanol present after centrifugation and drying (Figure S7a). Over time, the nanosheet pellet experienced a gradual but minimal mass loss on the order of 5%. As the decomposition temperature of bulk FeOCl in inert atmosphere is roughly 543 K, it is likely that the observed mass loss is caused by the proximity of the testing conditions to this temperature.³¹ While the observed mass loss is significant, the post-heating pXRD pattern of the nanosheet pellet (Figure S7b) aligns well with that of Li_xFeOCl, suggesting that decomposition of the nanosheet pellet itself was not extensive, albeit the degree of crystallinity was lowered.

When it was heated in air under high relative humidity, the nanosheet suspension gradually changed color from the purplebrown observed for representative FeOCl nanosheets to red, further indicating decomposition of the nanosheets under high relative humidity. When it was heated in air under low relative humidity, the nanosheet suspension was also observed to change color from purple-brown to red, but over a much longer period of time than the high relative humidity exfoliated suspension. The pXRD pattern of the decomposed nanosheet solution after drying shows that the sample decomposed to Fe₂O₃ (Figure S8).

Magnetic Characterization. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility measurements of polycrystalline FeOCl are in relative agreement with previously published results (Figure 4a).^{32,33} The Néel temperature, below which FeOCl should order antiferromagnetically, has

been reported to be in the range of roughly 84 K³² to 92 K.¹⁹ In this study, the $1/\chi$ vs T plot (Figure S9a) shows a broad transition centered at 84.6 K, which is where the $d\chi/dT$ plot (Figure S10) crosses zero. The broad transition from antiferromagnetic character to paramagnetic behavior observed in this region is likely related to the powder nature of the samples studied here, as the transition has been observed to be sharper in previous single-crystal studies.^{32,33} The nonlinear behavior of the inverse susceptibility at high temperatures, which violates the Curie-Weiss law, also agrees with the reported magnetic data of bulk FeOCl (Figure S9a). The observed magnetic moment at room temperature was found to be 2.79 $\mu_{\rm B}$ (Figure S11), similar to that reported previously $(2.76 \mu_{\rm B})$ but lower than that expected for high-spin Fe³⁺ (5.96 $(\mu_{\rm B})^{20}$ However, the large susceptibility observed at temperatures below 50 K disagrees with published results^{32,33} and likely originates from a minor iron oxide impurity phase. This impurity is not apparent in the XRD patterns or EDX spectra of representative bulk FeOCl samples, suggesting that it is quite small and largely amorphous. The presence of such a strongly magnetic impurity may also conceal the antiferromagnetic to paramagnetic transition, as well as produce the slight deviations from reported behavior at higher temperatures.³³ This is also supported by field-dependent magnetization measurements on the bulk, polycrystalline FeOCl. At 2 K, there is a slight curvature to the magnetization curve, indicating the presence of a small ferromagnetic impurity, but at 300 K no such curvature is evident, suggesting that it is not ferromagnetic at room temperature (Figure 4a). This minor impurity is removed during the centrifugation step of the exfoliation and therefore does not affect the studies of the nanosheet pellet.

Upon lithiation, the magnetic character of FeOCl is found to change significantly, exhibiting a new magnetic transition in the ZFC curve around 9 K, above which Li, FeOCl is shown to display a decrease in magnetic susceptibility more linear than previously reported. Although linear in the higher-temperature region, the lithiated material does not follow the Curie-Weiss law (Figure S9b), although Curie-Weiss behavior could be obscured by the presence of a small ferromagnetic impurity. The magnetic moment at room temperature was found to be 5.58 $\mu_{\rm B}$, unlike that in bulk FeOCl, and agrees better with the expected magnetic moment of high-spin Fe³⁺ (5.96 $\mu_{\rm B}$).²⁰ However, since the magnetic moment is so strongly temperature dependent (Figure S12) and decreases with temperature (similar to that in bulk FeOCl), we believe that the magnetic moment for this sample cannot be derived reliably. Impurities may also have an effect on the observed magnetic moment, as

is supported by the field-dependent magnetization data shown below. The ZFC magnetic behavior of the lithiated material roughly agrees with the previous investigation by Sagua et al.²⁴ In this study, the authors saw a slight reduction in susceptibility below 25 K, which is higher than the transition temperature observed in the current study. Furthermore, in our study a more pronounced drop in susceptibility is observed. Similar to the previous study, we find an increase in magnetic susceptibility upon intercalation. While previously it was argued that this increase can be explained by the reduction of Fe(III) to Fe(II) upon Li intercalation, we doubt that this explanation is warranted. The susceptibility increases by 1 order of magnitude, which is much too high to be explained by a change in Fe oxidation state. We find three more plausible scenarios: (1) The increase in susceptibility could be caused by a change in the magnetic ground state from AFM to canted AFM, which would result in a net moment. This is supported by the observed divergence of the FC and ZFC susceptibility curves. (2) Partial decomposition of the sample upon treatment with n-butyllithium, resulting in less antiferromagnetic FeOCl and more of the ferromagnetic impurity being present in the sample, could cause an increase in susceptibility. This option is also supported by the field-dependent magnetization discussed below. (3) A smaller particle size in the lithiated sample in comparison to the unlithiated sample, which could be caused by the aggressive n-butyllithium method of lithium intercalation, could also contribute to a higher observed moment.³⁴ While we also observe an increase in susceptibility upon lithiation, the total increase is significantly smaller than that reported by Sagua et al., which hints at the presence of different amounts of impurity phases or different particle sizes in the lithiated samples. Field-dependent magnetization measurements on the polycrystalline Li_xFeOCl at 2 K exhibit hysteresis not present in measurements conducted at 300 K (Figure 4b), suggesting some ferromagnetic character of the material when it is cooled to this temperature. At 300 K, the magnetization loop is seen to be S-shaped, to an extent greater than that seen in the 300 K magnetization loop for the bulk FeOCl, again indicating the presence of a ferromagnetic impurity.

To investigate the magnetic properties of the FeOCl nanosheets, we conducted FC and ZFC magnetic susceptibility measurements of the FeOCl nanosheet pellet, similarly to those performed in other studies of chemically exfoliated magnetic nanosheets.^{4,8} We observe a reduction in the magnitude of the magnetic susceptibility, roughly to the scale of that observed for bulk FeOCl, suggesting that the impurity previously present was removed by centrifugation. A new magnetic transition around 14 K is visible in the ZFC magnetic susceptibility curve but absent in the FC curve, a behavior that is often indicative of canted antiferromagnetism. Both the FC and ZFC measurements suggest Curie-Weiss behavior for the pellet (Figure S9c). Curie-Weiss fits show that the FeOCl nanosheet pellet has a Curie constant of C = 1.10 ± 0.06 , a Weiss temperature of θ = -340.1 ± 9.8 K, and an effective magnetic moment of $\mu_{\rm eff}$ = 2.98 ± 0.07 $\mu_{\rm B}$. This moment is close to that of bulk FeOCl, suggesting that the sheets might exhibit similar short-range magnetic order. This also supports the removal of the previously present impurity. The errors for these values were determined using the results of multiple measurements on different exfoliated samples. Nonetheless, we wish to point out that, if an impurity would still be present in the sample, the Weiss temperature could be significantly affected. However, since the observed magnetic moment agrees with that observed for bulk FeOCl, and the susceptibility remained constant over several sample batches (whereas it was found to be much higher for the decomposed sheets), we believe this to be unlikely. The large negative Weiss temperature indicates that the nanosheet pellet is magnetically frustrated. The frustration index, $f = \theta_{\rm CW}/T_{\rm N}$ (where $\theta_{\rm CW}$ is the Curie–Weiss temperature derived from the Curie–Weiss fitting and $T_{\rm N}$ is the transition observed at around 14 K), for this system is 24.29 ± 0.71; compounds with a frustration index greater than 10 are generally considered to be magnetically frustrated.³⁵

Field-dependent magnetization measurements on the FeOCl nanosheet pellet at 2 K exhibit hysteresis not present in measurements conducted at 300 K, but of a lesser magnitude in comparison to that observed in the Li_x FeOCl sample at 2 K (Figure 4c). The lack of hysteretic character in the 300 K *M* vs *H* loop would suggest that centrifugation of the exfoliation suspension was sufficient to remove the strongly magnetic impurity observed in both the bulk and lithiated FeOCl samples. The hysteresis exhibited by the pellet at 2 K, as well as the branching of the FC and ZFC curves at low temperatures, also support that canted antiferromagnetic character may be intrinsic to the nanosheet pellet.

All magnetic measurements conducted on the FeOCl nanosheet pellet could be reproduced across different batches of samples and differ significantly from those conducted on a representative decomposed FeOCl nanosheet pellet (Figure S13). While the magnetic properties observed for the nanosheet pellet are not necessarily representative of those intrinsic to an FeOCl monolayer, our results point to the existence of magnetic order in the sheets as well. As the pellet is turbostratically disordered, and thus interlayer interactions are weakened, its magnetic properties would be expected to more closely resemble those of a monolayer nanosheet than those of the bulk.⁴

CONCLUSION

We report the synthesis and physical characterization of thinlayer, roughly 0.5–1.0 μ m across FeOCl nanosheets, as well as magnetic characterization of the nanosheet pellet. TEM and AFM measurements show that when they are prepared under low relative humidity, relatively uniform, crystalline, thin-layer nanosheets may be produced. Magnetic measurements show that the nanosheet pellet retains the antiferromagnetic character intrinsic to the bulk FeOCl system and has a similar magnetic moment but, unlike its bulk parent, follows the Curie–Weiss law, has a lower transition temperature, and likely exhibits magnetic frustration.

Further studies on this system should focus on the understanding of the magnetic properties of single nanosheets. A similar synthetic approach may be used in the future toward the production of additional two-dimensional magnetic systems from the transition-metal oxychloride family.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b02856.

Experimental details, bulk FeOCl and Li_xFeOCl SEM data, additional TEM data, AFM data, TGA data,

decomposed FeOCl nanosheet pellet XRD data, and additional magnetic data (PDF)

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Notes

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