Strong anisotropy in the mixed antiferromagnetic system Mn$_{1-x}$Fe$_x$PSe$_3$

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We report the magnetic phase diagram of Mn$_{1-x}$Fe$_x$PSe$_3$ which represents a random magnet system of two antiferromagnetic systems with mixed spin, mixed spin anisotropies, mixed nearest neighbor magnetic interactions and mixed periodicities in their respective antiferromagnetic structure. Bulk samples of Mn$_{1-x}$Fe$_x$PSe$_3$ have been prepared and characterized phase pure by powder X-ray and neutron diffraction and X-ray fluorescence. Nature and extent of magnetically ordered state has been established using powder neutron diffraction, dc magnetic susceptibility and heat capacity. Long-range magnetic ordering exists between $x = 0.0$ and $0.25$ (MnPSe$_3$-type) and between $x = 0.875$ and 1 (FePSe$_3$-type). A short-range magnetic order with existence of both MnPSe$_3$- and FePSe$_3$-type nano-clusters has been established between $x = 0.25$ and 0.875. Irreversibility in dc magnetization measurements, also characterized by isothermal and thermoremanent magnetization measurements suggest similarities to magnetic nanoparticles where uncompensated surface spins result in a non-zero TRM and IRM response, further reinforcing existence of magnetic nano-clusters or domains. A spin glass state, observed in analogous Mn$_{1-x}$Fe$_x$PS$_3$ has been ruled out and formation of nano-clusters exhibiting both ordering types results from unusually high anisotropy values. The effect of ligand contributions to the spin-orbit interactions has been suggested as a possible explanation for high $D$ values in these compounds.

I. INTRODUCTION

Disrupting the long-range ordering of magnetic systems can manifest a variety of behaviors in crystalline materials, perhaps most notably in the form of emergent properties such as unconventional superconductivity in iron-based and cuprate materials. In those cases, the spin interactions are complex, with a mixture of local and itinerant moments and quantum fluctuations, respectively, leading to complex behavior. The superconducting parent compounds could be contrasted with materials where the behavior is more pedestrian, such as strongly classical systems where spin-glass behavior arises as multiple competing order parameters lead to a frozen state. A third, uncommon scenario can occur when the local coupling is strong enough to preclude the spin glass state, and competition can lead to uncompensated moments via complex domain formation.

A detailed mean-field and renormalization-group study of the possible magnetic orderings of randomly-mixed magnets was conducted by Fishman and Aharony in 1978. A random magnet containing a mixture of ions with competing spin anisotropies orders in a “mixed phase” or “oblique antiferromagnetic phase” at intermediate compositions and the phase diagram of such a magnet exhibits a tetracritical “decoupled” point. Experimental evidence of such phases has been observed in the solid-solution intermetallic Th$_8$Er$_{1-x}$Ni$_8$ and ionic Fe$_{1-x}$Co$_2$Cl$_2$. On the other hand, mixtures of antiferromagnets with different periodicities can form an intermediate phase with both magnetic orderings, as observed in Fe$_{1-x}$Mn$_x$WO$_4$. A random magnet with competing interactions forms a disordered or spin glass state as observed in Mn$_{1-x}$Fe$_x$PS$_3$.

Fe$_{1-x}$Mn$_x$WO$_4$ displays a very rich magnetic phase diagram where MnWO$_4$ exhibits 3 types of antiferromagnetic ordering and FeWO$_4$ exhibits only 1 type. A solid solution between the two results in competition between and a coexistence of interpenetrating magnetic structures related to the pure systems MnWO$_4$ and FeWO$_4$.

Two such compounds that exhibit different magnetic interactions and orderings are MnPSe$_3$ and FePSe$_3$ belonging to the family of metal thio(seleno)phosphates.

![Figure 1](image-url) (a,b) Crystal structure of MnPSe$_3$ and FePSe$_3$ with views along the a and c axes, where the octahedrally-coordinated $M^{2+}$ cations are shown in blue, S in yellow, and P in grey. (c,d) shows the magnetic structures for MnPSe$_3$ and FePSe$_3$, respectively. The direction of the Mn$^{2+}$ moments in the basal plane was recently found to be canted 8° from a[1].
(MTPs), which are two-dimensional layered compounds with layers bound by weak van der Waals forces. MTPs form a unique family of compounds in which the spin dimensionality may be varied by the choice of the transition metal ion. The MTPs were first discovered by Friedel in 1984[10] MnPSe$_3$ and FePSe$_3$ are isostructural and crystallize in $R3$ space group. Mn$_2$P$_2$Se$_6$ can be visualized as repeating slabs of SeM$_2$_0(P$_2$)$_{1/3}$Se in Cdl$_2$ structure type with 2/3 of the edge-sharing octahedral centers occupied by the transition metal anions, forming a honeycomb network, and the remaining 1/3 occupied by the P-P dimers as shown in Figure 1. The Se atoms' planes stack in an $ABAB$ sequence along $c$ axis. P-P dimers covalently bond to six Se atoms to form (P$_2$Se$_{6}$)$^{-4}$ ethane-like units.

The magnetic structures for MnPSe$_3$ and FePSe$_3$ were first examined in 1981 using neutron powder diffraction by Wiedenmann, et al[10] MnPSe$_3$ and FePSe$_3$ both order antiferromagnetically with $T_N$ of 74 and 119 K and Neel vectors $k = [000]$ and $k = [1/2 0 1/2]$, respectively. The magnetic moments of Mn$^{2+}$ ($S = 5/2$) lie in the basal plane all three intralayer $J1$ (n), $J2$ (nn) and $J3$ (nnn) interactions are antiferromagnetic. The direction of the moments in the basal plane is not known. On the other hand, the magnetic moments of Fe$^{2+}$ ($S = 2$) lie along $c$-axis with $J1$ being ferromagnetic, and $J2$ and $J3$ being antiferromagnetic. MnPSe$_3$ and FePSe$_3$ can thus be represented as Heisenberg XY and Ising systems, respectively. A solid solution between MnPSe$_3$ and FePSe$_3$ thus represents a quite complex random alloy, where $S$, $J$, $D$ and $k$ are all competing. Such a competition can result in presence of one or more of the theoretically predicted and experimentally realized magnetically ordered phases depending on the chemical composition. Magnetic ordering can, therefore, be glassy in case of strong competing exchange interactions as observed in sulfides, or be a competing two-phase ordered state in case of strong anisotropic contributions to the total Hamiltonian.

In this article, we present a detailed investigation of the magnetic phase diagram of Mn$_{1-x}$Fe$_x$PSe$_3$ by means of X-ray diffraction, X-ray Fluorescence, powder neutron diffraction, DC magnetization and heat capacity measurements. Our investigation reveals presence of the two end-member magnetic orderings along with a region of competing antiferromagnetic orders that exhibits uncompensated moments and nanoscale domains, as evidenced by broad magnetic diffraction peaks, despite sharp structural Bragg peaks.

II. EXPERIMENTAL PROCEDURE

Bulk synthesis of the samples in the solid solution range of Mn$_{1-x}$Fe$_x$PSe$_3$ ($0 \leq x \leq 1$, in increments of 0.125) was carried out using traditional solid state synthesis. Handling of Mn (Alfa Aesar, 99.98%), Fe (Alfa Aesar, 99%), P (Sigma-Aldrich, 99.99%) and Se (Alfa Aesar, 99.999%) reagents was performed in an Ar-filled glove box. Pre-cursors were loaded in 12 mm diameter fused silica tubes and sealed under vacuum using liquid nitrogen to prevent P and Se loss during vacuum sealing and reacted at 650°C with a ramp rate of 10°C per minute and 30 days hold time, followed by furnace cooling.

Powder X-ray diffraction measurements were conducted in transmission with a Bruker DS diffractometer with Mo-Kα radiation. Rietveld analysis was carried out using TOPAS 5[11] XRF data were collected using a Shimadzu EDX-7000 spectrometer under a He atmosphere. Three sets of data were collected and averaged to determine the composition.

Neutron diffraction data were collected between 1.5 K and 300 K using the HB-2A powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory for $x = 0, 0.25, 0.375, 0.5, 0.625$ and 1. Powders (1-2 g) were loaded in V cans with He exchange gas and measured with incident neutrons with wavelength $\lambda = 2.41$ Å. Rietveld analyses and magnetic structure solutions were performed with FullProf and SARA[12,13].

Magnetic susceptibility measurements were collected on a Quantum Design MPMS 3 magnetometer. Thermoremanent magnetization (TRM) and isothermal remanent magnetization (IRM) measurements were also collected on a Quantum Design MPMS 3 magnetometer.

The samples were field-cooled to 5 K, the temperature was stabilized for 10 min, field was turned off and the remanent moment was measured at the varying fields. For IRM measurements, the samples were cooled in zero field to 5 K, the temperature was stabilized for 10 min, a magnetic field was applied for 10 min and switched off, and remanent magnetic moment was measured. Heat capacity measurements were performed using a Quantum Design Dynacool PPMS (Physical Property Measurement System), with pressed pellets mounted using N-grease and a two-tau procedure.

III. RESULTS AND DISCUSSION

A. Evaluating structure and long-range order

Laboratory powder X-ray diffraction patterns for all compositions in Mn$_{1-x}$Fe$_x$PSe$_3$ at room temperature are shown in Figure 2. The Rietveld refinements for the diffraction patterns indicate that all synthesized compositions are phase pure. Due to the long annealing times (30 days) and the consistent peak width of reflections at high $Q$, it is apparent that the cation ordering is random and relaxed. However, the occupancies of Mn and Fe are indistinguishable by X-ray diffraction analysis and were refined separately by neutron diffraction. The Mn/Fe ratios obtained from XRF data are plotted in Figure 3 and slightly overestimate the Fe content by less than 10%. The XRDF-refined chemical contraction of the unit cell from MnPSe$_3$ to FePSe$_3$ varies smoothly, with a total change of about 4% in $a$ and 2% in $c$. This provides a consistent picture that the individual samples are truly a solid solution.
Figure 2. Room-temperature X-ray diffraction patterns of Mn$_{1-x}$Fe$_x$PSe$_3$ show consistent formation of the same structure type, without impurities, and with consistent peak width. The refinement to the FePSe$_3$ end member with the difference curve is shown.

Figure 3. Lattice parameters (a) refined from neutron diffraction data show linear variations from Mn/Fe substitution. In (b), agreement within 5% is seen in the neutron-refined Mn/Fe occupancies and the Mn/Fe ratio obtained from XRF. Taken together, the data indicate a random solid solution. Error bars are smaller than symbols in all cases.

Magnetic susceptibility measurements for all compositions in Mn$_{1-x}$Fe$_x$PSe$_3$ are shown in Figure 4. For low-dimensional systems, the value of $T_N$ as measured by specific heat is not always directly correlated to the maximum in the susceptibility versus $T$, and a broad maximum above $T_N$ is caused by short-range spin correlations. Here the $T_N$ from heat capacity (Figure 5) is more closely tracked by the point where the slope of the $\chi - T$ curve is maximized. The heat capacity of the $x = 0.5$ sample shows no lambda anomaly, although the general features of the susceptibility vary smoothly with $x$.

Figure 4. Magnetic susceptibility under zero-field cooling and field cooling with $H = 100$ Oe for all samples in the Mn$_{1-x}$Fe$_x$PSe$_3$ range. The most apparent proxy for Neel temperature is the maximum in susceptibility $T_{\text{max}}$, evident for each curve. Only samples from $x = 0.375$ to 0.625 show irreversibility, as evidenced in deviation of the ZFC and FC susceptibilities.

Figure 5. Heat capacity of the end members (a) MnPSe$_3$ and (b) FePSe$_3$ display clear peaks at the first-order $T_N$. The peak in MnPSe$_3$ is weaker due to the lack of orbital contribution when $S = 5/2$. At $x = 0.5$, the transition is broadened due to slow growth of nano-sized competing magnetic domains, but the total contribution can still be extracted from the Debye fits.
Curie-Weiss temperatures $\theta$ and effective magnetic moments ($\mu_{\text{eff}}$) were extracted from the susceptibility over the 280-400 K temperature range. The $\theta$ values are negative and summarized in Table I indicating short-range antiferromagnetic interactions in all compositions, and quite strong $\theta = -146$ K in MnPSe$_3$, which gradually weakens with Fe substitution. The effective magnetic moments $\mu_{\text{eff}}$ of MnPSe$_3$ (5.9$\mu_B$) and FePSe$_3$ (5.2$\mu_B$) indicate that both Mn$^{2+}$ and Fe$^{2+}$ are present in a high-spin state with $S = 5/2$ and $S = 2$. The $\mu_{\text{eff}}$ off all compounds agree roughly with the ideal values, except for the $x = 0.875$ and $x = 1$ samples, where $T_{\text{max}}$ is sufficiently high that strict adherence to Curie-Weiss behavior is not expected below 400 K.

Splitting between the ZFC and FC susceptibilities in Figure 4 is only observed from $x = 0.375$ to $x = 0.75$ and occurs around 40 K. The onset of this irreversibility is denoted $T_{\text{spin}}$ in Table I and suggests uncompensated spins that arise at boundaries of domains with dissimilar magnetic orderings, so it is not evident in the end members. The uncompensated surface spins of the domains can behave in a glassy or disordered way. The highest degree of irreversibility is observed as $x$ approaches 0.5 suggesting a higher uncompensated surface contribution form magnetic domains in intermediate compositions.

The total heat capacity measurements in Figure 5 only display an obvious $\lambda$ anomaly for the end members MnPSe$_3$ and FePSe$_3$, but even fitting the $x = 0.5$ sample to the Debye model reveals a gradual onset of magnetic ordering. The large peak in FePSe$_3$ (compared to MnPSe$_3$) can be explained by the magnetoelastic contribution from spin-orbit coupling, as was suggested for FePSe$_3$. Furthermore, the magnetic frustration as viewed by a larger Curie-Weiss $\theta$ versus the susceptibility $T_{\text{max}}$ indicates that MnPSe$_3$ is frustrated, and slowly orders with increasing domain size upon cooling. This is reflected in the deviation of $C_p$ versus the Debye fit in Figure 5(a).

The total heat capacity at low temperatures is a combination of electronic, lattice and magnetic contributions $C_{\text{total}} = C_{\text{elec}} + C_{\text{latt}} + C_{\text{mag}}$, where $C_{\text{elec}}$ is $\gamma T$, $C_{\text{latt}}$ is $\beta T^3 + \alpha T^5$. The fit to the heat capacity at low temperatures ($7 - 10$ K) was made using $C_{\text{latt}}$ since these chalcogenides are insulators with high resistivity of the order of $10^6$ $\Omega\cdot$m to estimate Debye temperatures. The high-temperature heat capacity data was then fit using the Debye model to better estimate $C_{\text{latt}}$ and Debye temperatures. $C_{\text{mag}}$ was calculated by $C_{\text{total}} - C_{\text{latt}}$ and $C_{\text{mag}}/T$ vs $T$ plot was integrated to give the entropy associated with the magnetic transition. The theoretical limit to the statistical magnetic entropy for complete ordering of Mn$^{2+}$ ($S = 5/2$) should be $R \ln(2S + 1) = 14.89$ $J \cdot mol^{-1} \cdot K^{-1}$ and of Fe$^{2+}$ ($S = 2$) should be 13.38 $J \cdot mol^{-1} \cdot K^{-1}$. It is clear from Figure 5 that the Mn$_{1-x}$Fe$_x$PSe$_3$ does precisely track Debye-like behavior, as is typical for similar materials, but rough agreement is seen: The entropy calculated for $x = 0.0, 0.5$ and 1.0 amount to 13.84 $J \cdot mol^{-1} \cdot K^{-1}$, 13.23 $J \cdot mol^{-1} \cdot K^{-1}$ and 10.73 $J \cdot mol^{-1} \cdot K^{-1}$ with respective Debye temperatures of 235 K, 240 K and 250 K. These values indicate that the ordering in intermediate compositions is still transitioning from states that are nearly fully disordered to fully ordered over the measured temperature range.

### B. Progression of magnetic ordering across the Mn$_{1-x}$Fe$_x$PSe$_3$ compositional range

Our refined neutron powder diffraction data at $T = 1.5$ K is shown for the end members MnPSe$_3$ and FePSe$_3$ in Figure 6. We verify the magnetic propagation vectors $k = [000]$ and $k = [100]$, respectively. The average magnetic moments on Mn$^{2+}$ and Fe$^{2+}$ in the end members were refined to 3.6 $\mu_B$ and 4.2 $\mu_B$, respectively. The direction of the Mn$^{2+}$ moments can not be determined from powder diffraction data.

Smaller calculated magnetic moment can be attributed to lack of information about the direction of magnetic moments or lack of long range magnetic order in MnPSe$_3$. Magnetic structure of the analogous sulfides have been subjects of recent controversy. The magnetic structure of MnPSe$_3$ was identified with a propagation vector of $k = [000]$ where the Mn$^{2+}$ moments lie at a finite angle of 8°C from $c^\star$ axis as compared to the previously published magnetic structure where the magnetic moments are along $c^\star$. If we assume similar magnetic ordering in MnPSe$_3$ and MnPS$_3$, Rietveld analysis with Mn$^{2+}$ lying in the $ab$ plane could cause the calculated magnetic
Table I. Expected values and measured parameters from magnetic susceptibility measurements and fits to Curie-Weiss behavior ($\mu_{\text{eff}}$ and $\theta$).

| $x$ in Mn$_{1-x}$Fe$_x$PSe$_3$ | $S_{\text{ideal}}$ | $\mu_{\text{eff,ideal}}$ ($\mu_B$) | $\mu_{\text{eff,expt}}$ ($\mu_B$) | $\theta$ (K) | $T_{\text{max}}$ (K) | $T_{\text{split}}$ (K) |
|-----------------------------|---------------------|-------------------------------------|------------------------|-------------|------------------|------------------|
| 0.000                       | 5/2                 | 5.92                                | 5.90                   | -146        | 84               | -                |
| 0.125                       | 2.44                | 5.79                                | 5.98                   | -150        | 70               | -                |
| 0.250                       | 2.38                | 5.66                                | 5.98                   | -130        | 61               | -                |
| 0.375                       | 2.31                | 5.54                                | 5.68                   | -97.7       | 63               | 40               |
| 0.500                       | 2.25                | 5.41                                | 5.76                   | -88.6       | 40               | 40               |
| 0.625                       | 2.19                | 5.28                                | 4.82                   | -56.6       | 73               | 46               |
| 0.750                       | 2.13                | 5.15                                | 4.93                   | -39.7       | 105              | 43               |
| 0.875                       | 2.06                | 5.03                                | 5.43                   | -28.3       | 113              | -                |
| 1.000                       | 2.00                | 4.90                                | 5.24                   | -8.86       | 124              | -                |

Figure 7. Evolution of magnetic ordering peaks with temperature and composition. The nuclear fits have been shown in black to clearly identify magnetic intensities at various temperatures. Peaks corresponding to FePSe$_3$-type and MnPSe$_3$-type magnetic ordering have been highlighted in blue and pink respectively. Presence of broad diffuse magnetic peaks caused by short-range order is seen in intermediate compositions as compared to sharp magnetic peaks in end members.

Across the compositional range, a few key changes should be noted in the neutron diffraction patterns at 1.5 K, shown in Figure 7. First, the magnetic reflections in FePSe$_3$ are clearly broadened (and although it is more subtle, there is substantial diffuse scattering from magnetic intensity in MnPSe$_3$), and there is a progression of mixing and broadening of the magnetic Bragg contributions from both phases as intermediate values of $x$ are examined.

In FePSe$_3$, the broadening of the 011 magnetic reflection is not immediately apparent from Figure 7 but upon closer inspection in Figure 8, it is significant and can be
refined as a Voigt contribution corresponding to a correlation length \( L = 600 \pm 200 \) Å, and remains broad at \( T = 70 \) K to \( L = 500 \pm 100 \) Å. This peak broadens further into a diffuse, but still detectable, contribution at 150 K, which is higher than \( T_N = 124 \) K for FePSe\(_3\), indicating short-range magnetic correlations that are common for low-dimensional materials\(^{15,16}\). For a higher-angle \( \bar{1}21 \) magnetic peak, the correlation lengths are not determinable within the limits of instrumental and sample broadening.

In other magnetic compounds with strong crystalline anisotropy such as such as Sr\(_2\)YRuO\(_6\)\(^{21}\), CrTa\(_2\)O\(_6\)\(^{22}\) and La\(_2\)O\(_3\)Mn\(_2\)Se\(_2\)\(^{23}\), magnetic domains that exhibit strong correlations in two dimensions above 3D long range magnetic transition temperature are typically modeled by Warren-type peaks\(^{22}\), which are characterized by long tails with increasing \( Q \), similar to turbostratic nuclear disorder in layered compounds and clays. While the layered structure of Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\) could play host to such disorder, we observe neither nuclear disorder nor Warren-type tails on the magnetic peaks. Instead, the magnetic peaks are best described as lorentzian contributions after instrumental and crystallite size corrections (Figure 8). This implies that the short range ordering present in Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\) has a significant interplane component, unlike other 2D materials such as Sr\(_2\)YRuO\(_6\), CrTa\(_2\)O\(_6\) and La\(_2\)O\(_3\)Mn\(_2\)Se\(_2\). This behavior is corroborated by the fact that the broad magnetic peaks correspond to \( hkl \) family of planes, instead of \( h0k \).

For samples where \( 0.675 \leq x \leq 0.375 \), magnetic peaks are broadened and the two \( k \)-vectors coexist. The extracted correlation lengths for these with varying composition and temperature are plotted in Figure 9. Interestingly, only the FePSe\(_3\) end member at \( x = 1 \) shows domain sizes that are large enough that the peaks are not broadened versus the nuclear peaks. Correlation lengths drop more steeply for FePSe\(_3\)-type ordering as compared to MnPSe\(_3\)-type ordering for intermediate compositions. This could be explained by stronger anisotropic and hence less susceptible character of MnPSe\(_3\) as compared to FePSe\(_3\).

C. Nature of and driving forces for the coexistence of magnetic domains

It is clear from the susceptibility and diffraction measurements that Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\) exhibit mixed magnetic ordering below \( T_N \). The layers containing magnetic cations are separated by a van der Waals gap on the order of \( \sim 7 \) Å, which prohibits direct exchange and super exchange interactions between layers. The intralayer neighboring magnetic interactions are much stronger, as evidenced by the non-Curie-Weiss behavior and diffuse magnetic scattering above \( T_N \). Clearly, the differences between this system and other mixed magnets (which typically result in spin glasses) should be understood. For a random cation mixture on Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\), a Hamiltonian for the spin interactions can be written:

\[
H = -2J_{Mn} - 2J_{Fe} - 2J_{MnFe} - D_{Mn} - D_{Fe},
\]  
(1)
where,

\[ J_{Mn} = J_{MnMn} \sum_{<i,j>} \vec{S}_{Mn_i} \cdot \vec{S}_{Mn_j}, \]

\[ J_{Fe} = J_{FeFe} \sum_{<k,l>} \vec{S}_{Fe_k} \cdot \vec{S}_{Fe_l}, \]

\[ J_{MnFe} = J_{MnFe} \sum_{<p,q>} \vec{S}_{Mn_p} \cdot \vec{S}_{Fe_q}, \]

\[ D_{Mn} = D_{Mn} \sum_i (S^z_{Mn_i})^2, \]

\[ D_{Fe} = D_{Fe} \sum_k (S^z_{Fe_k})^2 \]  

(2)

\[ H = -2J_{MnMn} \sum_{<i,j>} \vec{S}_{Mn_i} \cdot \vec{S}_{Mn_j} - 2J_{FeFe} \sum_{<k,l>} \vec{S}_{Fe_k} \cdot \vec{S}_{Fe_l} \]  

(3)

Here, \( J \) are exchange interactions between two neighboring magnetic ions and \( D \) denotes the anisotropy. \( D_{Mn} < 0 \) and \( D_{Fe} > 0 \) for MnPSe\(_3\) and FePSe\(_3\) as per their Heisenberg and Ising nature, respectively. MnPSe\(_3\) is highly anisotropic as determined by single-crystal magnetic susceptibility measurements carried out by Jeevanandam\(^{22}\) with a single-ion exchange anisotropy of magnitude 26.6 \( K \), which is approximately five times the exchange interaction (−5.29 \( K \)). No comparable susceptibility measurement exists for FePSe\(_3\) to estimate the value of \( D \). However, the exchange interaction \( J_{FeFe} \) is of the similar magnitude (between 3.7 and 10.4 \( K \)) to that of MnPSe\(_3\) but ferromagnetic in nature as determined by Wiedenmann\(^{10}\). Assuming similar magnitudes of \( D_{Fe} \) and \( D_{Mn} \), the question is what ordered states are accessible by a random 2D-sheet mixture of these cations. Fishman and Aharony have provided theoretical models for random alloys of two antiferromagnets with different periodicities, different anisotropies and different interactions in separate studies\(^{11,14}\) but their results cannot be directly applied to our system which represents a combination of all three forms of competition.

A solid solution of analogous sulfides, on the other hand, results in a spin glass state at intermediate compositions\(^6\). Both MnPSe\(_3\) and FePSe\(_3\) order antiferromagnetically with spins normal to \( ab \) plane and \( k = [001] \) and \( k = [01\frac{1}{2}] \), respectively. In MnPSe\(_3\), each Mn\(^{2+}\) is antiferromagnetically coupled with its nearest neighbors in the plane and there is ferromagnetic coupling between the planes. In FePSe\(_3\), each Fe\(^{2+}\) is ferromagnetically coupled with two nearest neighbors and antiferromagnetically with the third one and forms zigzag spin chains coupled antiferromagnetically within each layer. MnPSe\(_3\) is magnetically isotropic with a very small anisotropy parameter of 0.105 \( K \), with exchange interactions of \( J_1 = -9.1 \) \( K \), \( J_2 = -0.83 \) \( K \) and \( J_3 = -2.15 \) \( K \)\(^{22}\). The nature of small anisotropy is debated between dipolar anisotropy and single ion anisotropy; however that does not effect our argument here. FePSe\(_3\), on the other hand, is anisotropic with single-ion anisotropy parameter \( D = 31.7 \) \( K \), approximately double the exchange parameters; \( J_1 = 17.4 \) \( K \), \( J_2 = -0.48 \) \( K \), \( J_3 = -11.4 \) \( K \)\(^{22}\).

The spin glass state in these random sulfides could be explained by competing antiferromagnetic and ferromagnetic exchange interactions within the plane in the presence of smaller competing anisotropies as compared to selenides. The dominating spin exchange interactions result in spin frustration with a formation of frozen or glassy state of spins as temperature is lowered in these systems\(^{21,22}\).

In contrast to Mn\(_{1-x}\)Fe\(_x\)PS\(_3\), the absence of a spin glass state in Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\) can be explained by a relatively larger contribution of \( D_{Mn} \) and \( D_{Fe} \) anisotropy terms as compared to the exchange interactions. The tendency to obey a particular magnetic ordering increases with increasing anisotropy. Even small local chemical clustering in a randomly mixed solid solution can change the spin dynamics and segregate the system into coexisting magnetic domains of the favored end members. Local regions rich in Mn\(^{2+}\) or Fe\(^{2+}\) type ions can continue to polarize the magnetic ordering in their vicinity resulting in a two-phase competition region between \( x = 0.25 \) and \( x = 0.875 \).

The anisotropy parameter \( D \), which introduces anisotropy in an otherwise isotropic Hamiltonian, arises from a combination of crystal-field and spin-orbit coupling\(^{23}\). Covalency parameter and spin-orbit coupling constant are both higher for selenium than for sulfur, which results in a higher spin-orbit interaction, which in turn has a substantial effect on zero-field splitting parameter \( D \). A large zero-field splitting of the transition metal in selenides results in an unusually large anisotropy in MnPSe\(_3\) as compared to MnPSe\(_3\). Differences in \( D \) in the EPR spectra of Cr\(^{2+}\) in cubic ZnS, ZnSe, and ZnTe\(^{22}\) has been explained by a similar argument.

Among the SG and 2-phase models that are possible ground states for such randomly-mixed 2D systems, each has its own tendency for formation based on \( J \) and \( D \) competition. The macroscopic response of these scenarios manifest in changes in the amount of uncompensated spins and their time-dependent susceptibility. Clearly, the spin glass scenario is ruled out of Mn\(_{1-x}\)Fe\(_x\)PSe\(_3\) due to the high amount of ordered moment observed in the neutron diffraction data, but additional confirmation can be seen in time-dependent magnetization measurements.

TRM and IRM curves for ideal bulk antiferromagnets should be zero\(^{31}\) and higher values of TRM versus IRM denote irreversibility as embodied in a spin-glass (evenly-distributed frozen spins) or nano-domain behavior with a large fraction of uncompensated surfaces, occasionally seen in core-shell nanoparticles. Both behaviors are shown schematically in Figure 10\(^{39}\) for a spin glass, the IRM increases with increasing field, then meets the TRM curve at moderate field values, where both then saturate. The TRM also exhibits a characteristic peak at intermediate fields. TRM-IRM curves for antiferromagnetic nanoparticles have been measured and show an increasing TRM and IRM with no signs of saturation, a behavior
that has been often compared to a 2D-DAFF response\cite{32}.

The thermoremanent and isothermal remanent magnetization (TRM and IRM) measurements at 5 K on Mn$_{1-x}$Fe$_x$PSe$_3$ for $x = 0.0$, 0.5, 1.0 are shown in Figure 10. TRM and IRM for $x = 0.0$ and 1.0 are negligible (ideal bulk antiferromagnets) as compared to those for $x = 0.5$. For $x = 0.5$, the IRM increases nearly linearly, but at a slower rate than TRM. TRM and IRM for $x = 0.5$ does not saturate at high magnetic fields and does not display a spin-glass behavior, but instead matches interface-dominated behavior, which is seen in systems with small magnetic domain sizes, for example in Co$_3$O$_4$ nanowires, where uncompensated surface spins lead to irreversibility in addition to the regular antiferromagnetic contribution from the wires.\cite{32} The decrease in correlation lengths of coexisting clusters of MnPSe$_3$ and FePSe$_3$ type ordering at intermediate compositions lead to more “uncompensated surfaces” with random ordering, which results in an increasing TRM and IRM.

The final magnetic phase diagram of Mn$_{1-x}$Fe$_x$PSe$_3$ is shown in Figure 11. The phase transition lines were drawn based on $T_{\text{max}}$ obtained from $\chi - T$ measurements. Between $x = 0.0$ and $x = 0.25$, MnPSe$_3$ type magnetic ordering is present with introduction of short range correlations as $x$ or Fe$^{2+}$ concentration is increased. $T_{\text{max}}$ decreases as $x$ increases and is minimum for $x = 0.5$. Between $x = 0.25$ and $x = 0.875$, mixed ordering or co-existence of Mn$^{2+}$ and Fe$^{2+}$-type ordering is present. The mixed phase forms nano-sized chemically disordered clusters which display both kinds of ordering. The uncompensated surfaces between the clusters increase as the cluster size decreases and the effect can be seen in TRM-IRM, ZFC-FC magnetization and neutron diffraction measurements. Cluster size decreases as a function of chemical disorder present and is smallest for $x = 0.5$. The absence of Schottky anomaly in heat capacity for $x = 0.5$ suggests short range ordering where the transition lines in the phase diagram defined by $T_{\text{max}}$ over intermediate compositions are not smooth and very well defined. For $x > 0.875$, FePSe$_3$ type magnetic ordering is present. The strong dependence of correlation lengths on the Fe$^{2+}$ concentration for $x > 0.5$ suggests a lower value of anisotropy $D_{Fe}$ as compared to $D_{Mn}$. This is also supported by weak dependence of correlation lengths on Fe$^{2+}$ concentration for $x < 0.5$.

IV. CONCLUSIONS

In conclusion, we have established a magnetic phase diagram of a mixed spin, mixed interaction, mixed anisotropy and mixed periodicity system Mn$_{1-x}$Fe$_x$PSe$_3$ using a combination of X-ray diffraction, X-ray Fluorescence, neutron diffraction, DC magnetic susceptibility, TRM, IRM and heat capacity measurements on bulk powder samples. This is the first solid solution study of a random magnet system in metal selenophosphates family. Both kinds of MnPSe$_3$ and FePSe$_3$ type ordering are found to co-exist at intermediate compositions in the form of nanosized clusters. FePSe$_3$ type ordering is found to be more susceptible to doping as compared to
the MnPSe$_3$ type ordering. A long range ordering does not take place in intermediate compositions up to 1.5 K and the broad diffuse scattering peaks are observed in neutron diffraction patterns. The magnetic ordering in intermediate compositions take place over a wide temperature range and does not display a characteristic lambda anomaly in heat capacity. The uncompensated surface spins increase with shorter correlation lengths and are evident in DC magnetization and TRM-IRM measurements. The mixed ordering can be explained by high values of $\Delta$ arising from ligand spin-orbit contributions. Future measurements involving single crystal neutron diffraction can be employed to establish the direction of moments withing the basal plane in MnPSe$_3$. Magnetic domain imaging such as lorentz microscopy and magnetic force microscopy can be used to further characterize and image the anisotropic nature of the domains.

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