Intrinsic exchange bias in Zn$_x$Mn$_{3-x}$O$_4$ ($x \leq 1$) solid solutions

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Bulk specimens of the heterolite solid solution Zn$_x$Mn$_{3-x}$O$_4$ with $x = 0, 0.25, 0.5, 0.75,$ and $1$ have been prepared as homogeneous, phase-pure polycrystalline samples as ascertained by neutron diffraction measurements. Samples with $x = 0.25, 0.5,$ and $0.75$ exhibit shifted magnetic hysteresis loops at low temperature, characteristic of exchange bias typically seen in magnetic composites. We propose that the unusual magnetic behavior arises as a result of a nanoscale mixture of ferromagnetic and antiferromagnetic regions that are distinct but lack long-range order. While some glassy behavior is seen in AC magnetic measurements, its magnitude is not sufficient to account for the observed dramatic exchange bias. Furthermore, isothermal and thermoremanent magnetization measurements distinguish this material from a pure spin glass. The title system offers insights into the alloying of a ferrimagnet Mn$_3$O$_4$ with an antiferromagnet ZnMn$_2$O$_4$ wherein distinct magnetic clusters grow and percolate to produce a smooth transition between competing orders.

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I. INTRODUCTION

Exchange bias is a magnetic memory effect that occurs at the interface between a ferromagnet (or ferrimagnet) and an antiferromagnet. By field-cooling a system with an ordered ferromagnet/antiferromagnet interface through the Néel temperature $T_N$ of the antiferromagnet, exchange interactions at the interface lead to a preferred direction of magnetization, typically along the cooling field direction. Exchange bias has been engineered into a wide variety of materials systems and geometries: core-shell nanoparticles, granular composites, and thin film read-heads for magnetic recording media. In addition to the abrupt interfaces in thin-film architectures, a significant thrust has been made toward understanding the mechanisms of loop-shifting phenomena in disordered and composite magnets.

Disordered and/or dilute magnetic spins in a crystal can lead to glassy behavior that gives rise to magnetic memory effects as a result of slow and time-dependent processes below the spin freezing temperature $T_f$. Such glassiness can result in biased magnetization loops. Distinctions between exchange bias and glassy magnetism are therefore useful. Exchange-biased systems are usually expected to have (i) two magnetic phases with a well-defined interface, (ii) a loop shift, measured as the exchange field, $H_E$, that goes to zero above $T_N$, and (iii) zero exchange field (loop shift) if the cooling field is zero; exchange bias is not observed for $M - H$ loops acquired after zero-field cooling. Spin glasses, in turn, are associated with (i) frozen spins below $T_f$ that produce a frequency-dependent peak in susceptibility, (ii) an absence of long-range magnetic ordering, and (iii) some relaxation on a macroscopic time scale after field changes below $T_f$. 

As an illustrative example, loop shifts along the field axis were observed in the prototypical spin glass CuMn by Monod, et al. in 1979 but these are not strictly considered to be evidence for exchange bias since the magnetic phase is homogeneous and field-cooling is not necessary. A glassy phase can occasionally fulfill the role of an antiferromagnet in a two-phase exchange biased system: loop shifts are commonly observed in ferromagnetic-core nanoparticles with disordered surface layers, where a spin-glass-like relaxation of the remanent magnetization versus time is accompanied by a loop shift. Glassy spins freeze to partially align with the ferromagnetic spins during field cooling and a preferred direction of magnetic orientation is therefore imparted. A detailed study of the interplay between ferromagnet/spin glass Co/CuMn bilayers with well-defined thicknesses has confirmed this behavior.

Here we report a detailed study of the magnetic properties of Zn$_x$Mn$_{3-x}$O$_4$ ($x \leq 1$) solid solutions, studied in phase-pure polycrystalline samples. This system was reported many decades ago by Jacobs and Kouvel who found that exchange bias and “magnetic viscosity” effects (meaning glassy magnetism in the current context) were found to occur together in the solid solution. We
At high temperatures, the orbital ordering patterns is observed.\textsuperscript{22,23}

\section*{II. Methods}

Ceramic pellets of Zn\textsubscript{x}Mn\textsubscript{3−x}O\textsubscript{4} were prepared by grinding stoichiometric amounts of ZnO and MnO (both 99.9 \% from Aldrich) in an agate mortar and pestle, pressing at 100 MPa, and firing in air at temperatures between 950°C and 1200°C for 24 h (water quenched for \(x = 0\) and 0.25) in accordance with the phase diagram of Driessens and Rieck.\textsuperscript{24} For all calcinations, pellets were buried in sacrificial powder of the same composition in covered alumina crucibles. The purity of all samples was confirmed by laboratory X-ray diffraction (XRD) data acquired on a Philips X’Pert diffractometer with Cu K\(_\alpha\) radiation. Magnetic properties were measured using a Quantum Design MPMS 5XL SQUID magnetometer. Time-of-flight (TOF) neutron powder diffraction on samples held in vanadium cans at the high intensity powder diffractometer (HIPD) at Los Alamos National Laboratory. The HIPD instrument can collect high \(d\)-spacing magnetic reflections out to tens of \(\AA\). However, no peaks were found beyond 6 \(\AA\) in any of the samples studied here. We limit the Rietveld refinement to banks 1–4, with a maximum momentum transfer \(Q_{\text{max}} = 20 \text{ } \AA^{-1}\) and maximum \(d\)-spacing of 6 \(\AA\). Rietveld refinement was performed using the XND code\textsuperscript{25} for X-ray data and GSAS\textsuperscript{26} for TOF data. Crystal structures are visualized using VESTA.\textsuperscript{27}

\section*{III. Results and Discussion}

Time-of-flight neutron diffraction is an especially useful tool in examining the solid solutions studied here. In addition to the possibility of variable temperature studies, the availability of high resolution high momentum transfer \((Q)\) data, the ability to probe magnetic scattering, and the ability to examine \(\text{Zn}^{2+}/\text{Mn}^{3+}\) A-site distribution are all advantageous. The nuclear scattering lengths are 5.68 fm for Zn and \(-3.73\) fm for Mn, so these ions are extremely well contrasted in the scattering.

Room temperature neutron TOF diffraction patterns are shown in Fig.\textsuperscript{3} along with fits to the profiles using the Rietveld refinement method. The fits give excellent matches to the heterolite structure across the solid solution. The TOF refinements reveal no impurities, and the particles are many microns in extent as seen from the narrow widths of the diffraction peaks. Structural parameters from the Rietveld refinement are provided in Table\textsuperscript{4} Trends in the relevant structural parameters as a function of \(x\) are shown in Fig.\textsuperscript{2}.

The cell volume and \(c/a\) ratios vary smoothly and reflect the 10 \% difference in the ionic radii of tetrahedral \(\text{Mn}^{2+}\) (0.66 \(\AA\)) and tetrahedral \(\text{Zn}^{2+}\) (0.60 \(\AA\)). The decrease in tetragonality as the Zn content \(x\) increases could be due to its preference for covalent bonding, and there-
fore a tendency toward more regular tetrahedral coordination. This is supported by the oxygen $y$ and $z$ coordinates, which approach their least-offset values of $\frac{1}{4}$ and $\frac{1}{2}$, respectively with increasing Zn. The oxygen $U_{\text{iso}}$ values for each compound are relatively close, but the smallest values occur for the end members, while site mixing on the A-site leads to larger values for intermediate $x$. Random A-site mixing of Zn$^{2+}$/Mn$^{2+}$ is suggested by the smoothly varying lattice parameters and the $c/a$ ratios versus $x$. This system strictly maintains a "normal" distribution of cations: Zn$^{2+}$ greatly prefers tetrahedral coordination by oxygen, and Mn$^{3+}$ is very stable in a JT distorted octahedral coordination. The A-site occupation refines to within 1% of the nominal Zn/Mn ratio in each case. The JT distortion is present in all samples since the B sublattice is invariant with composition $x$.

Figure 3 displays TOF diffraction patterns at $T = 300$ K, 50 K, and 20 K over a region that contains all magnetic scattering intensity relevant to the discussion here. Most obvious are the numerous, intense magnetic peaks in the end member Mn$_3$O$_4$. The top panel is on a log scale one order of magnitude higher than the rest. The onset of long-range magnetic ordering leads to a transfer of intensity from the diffuse scattering to the Bragg peaks, resulting in a much lower baseline for the 20 K data than that at higher temperatures. The magnetic structure of hausmannite Mn$_3$O$_4$ is complex, with the onset of incommensurate sinusoidal magnetic ordering at $T_C = 44$ K, followed by a locking in of the spin modulation to a commensurate structure below 33 K.

FIG. 1: 300 K neutron TOF diffraction Rietveld refinements in the $I4_1/amd$ space group confirm the purity of all Zn$_x$Mn$_{3-x}$O$_4$ phases at 300 K. Difference profiles are shown below each fit. Refinement results (including $R_{wp}$) are provided in Table I.

FIG. 2: Structural parameters at 300 K from neutron TOF Rietveld refinements show decreasing (a) $c/a$ ratios and (b) cell volume with Zn concentration (linear fits, dashed) due to its smaller radius. The oxygen $z$ position in (c) decreases toward the undistorted value of 0.25. In (d), chemical disorder causes compounds with intermediate Zn/Mn mixing to have higher thermal parameters than the end members. Error bars are smaller than the symbols in all panels.

FIG. 3: (Color online) Neutron TOF powder diffraction patterns (log scale, offset for clarity) for the Zn$_x$Mn$_{3-x}$O$_4$ solid solutions at 300 K, 50 K and 20 K. The Rietveld fit to the 300 K (non-magnetic) profile is shown for all samples. Note that only diffuse magnetic scattering is evident around $d = 5$ Å for the sample with $x = 0.5$. In Mn$_3$O$_4$, the baseline at 20 K drops due to transfer of diffuse magnetic scattering to Bragg peaks.
TABLE I: Bulk structural parameters at 300 K for Zn$_{2-2x}$Mn$_{3-2x}$O$_4$ obtained from Rietveld refinement of TOF neutron diffraction data: $I4_1/amd$ (No. 141, origin choice 2); A-site Zn$_{3-x}$Mn$_{1-x}$ at $(0,1/2,1)$; B-site Mn at $(0,1/2,1)$; O at $(0,y,z)$.

| Composition            | $a$ (Å) | $c$ (Å) | $c/a$ | $yO$ | $zO$ | $U_{iso}$ (Å$^2$) | $R_{wp}$ (%) |
|------------------------|---------|---------|-------|------|------|----------------|-------------|
| ZnMn$_2$O$_4$          | 5.71643(5) | 9.2275(1) | 1.1414 | 0.47657(8) | 0.25577(5) | 0.0060(2) | 3.1          |
| Zn$_{0.75}$Mn$_{2.25}$O$_4$ | 5.71955(3) | 9.28628(7) | 1.1481 | 0.47524(3) | 0.25681(2) | 0.00894(4) | 2.8          |
| Zn$_{0.5}$Mn$_{2.5}$O$_4$ | 5.73726(3) | 9.3504(1)  | 1.1524 | 0.47499(3) | 0.25751(2) | 0.00702(4) | 3.0          |
| Zn$_{0.25}$Mn$_{2.75}$O$_4$ | 5.75134(4) | 9.4225(1)  | 1.1585 | 0.47404(4) | 0.25867(3) | 0.00767(4) | 3.3          |
| Mn$_3$O$_4$             | 5.75924(2) | 9.46323(6) | 1.1622 | 0.47273(3) | 0.25913(2) | 0.00534(7) | 2.7          |

At the other end of the solid solution, heterolite ZnMn$_2$O$_4$ has fewer and weaker magnetic peaks. While extensive work has been done on the magnetic ordering of cubic spinels where the spins are confined purely on the B sublattice and are strongly geometrically frustrated, the magnetic ordering in tetragonally distorted hausmannite/hetærolite B-site compounds has received less attention. There are three relevant tetragonal spinels to consider: ZnMn$_2$O$_4$, CdMn$_2$O$_4$, and MgMn$_2$O$_4$. Zn and Cd both have a strong tendency to occupy tetrahedral sites, but Mg is exhibits about 10–25% inversion on the octahedral sites. No description of the magnetic structure has accompanied studies of (Zn,Cd)$_3$Mn$_{3-2x}$O$_4$. Interpretation of the hetærolite magnetic structure to consist of ferromagnetic chains of Mn$^{3+}$, with antiferromagnetic interchain interactions. This simple interpretation clearly does not capture all the details as is evident in the TOF neutron diffraction data, where the peaks in ZnMn$_2$O$_4$ are diffuse and therefore indicate a substantial amount of disorder over long length scales. There is a shift of intensity from the (101) peak at $d = 4.9$ Å once $x$ increases past 0.5, and the intensity of the diffuse peak at $d = 5.05$ Å gradually increases until ZnMn$_2$O$_4$ is reached. In the middle compound with $x = 0.5$, no magnetic Bragg peaks are present. There is only a slight increase in diffuse intensity around $d = 5$ Å, so any magnetic order at this point must only be short-range in nature.

While the magnetic neutron scattering data requires a more detailed analysis that will be presented in future work, we use the general trends to explain AC and DC magnetization measurements presented in this
work. DC magnetization measurements on members of the \( \text{Zn}_x\text{Mn}_3\text{O}_4 \) solid solution indicate a smooth, linear decrease in both the magnetic ordering temperature as well as the maximum magnetization on going from \( \text{Mn}_3\text{O}_4 \) (\( x = 0 \)) to \( \text{ZnMn}_2\text{O}_4 \) (\( x = 1 \)). The field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves in Fig. 5 show a steady decline in the ordering temperature, temperature of magnetic irreversibility (deviation of ZFC and FC curves), and FC moment as \( x \) goes from 0 to 0.75. The magnetization curves show that the neutron TOF data in Fig. 3 at 20 K is below \( T_C \) for the four ferrimagnetic samples. The samples at \( x = 0.5 \) and 0.75 have significant diffuse intensity at 50 K, well above \( T_C \) measured via SQUID magnetization. Interestingly, the weak magnetic scattering intensity in \( x = 0.5 \) versus \( x = 0.75 \) (Fig. 3) seems contradict the fact that \( x = 0.5 \) has the larger magnetization and higher \( T_C \). We can therefore assume that in \( x = 0.5 \) samples, ferrimagnetism is caused by local regions of aligned spins which lack long-range order.

The ZFC-FC behavior for \( \text{ZnMn}_2\text{O}_4 \) is much more complex than the other samples in the solid solution, and has been the subject of continued investigation for many years.\(^ {21} \) Salient features that have remained consistent are Curie-Weiss paramagnetism above room temperature, with a phase transition between 230 K and 290 K that has been detected in specific heat\(^ {21} \) and Young’s modulus\(^ {21} \) measurements. In our measurements of the ZFC/FC behavior in Fig. 6, we observe this as a gradual slope change in \( M^{-1} \) versus \( T \). The irreversible moment \( M_{\text{FC}} - M_{\text{ZFC}} \) has a slight dip around 260 K and a strong transition at 60 K. A new magnetic Bragg peak at \( d = 5.05 \text{Å} \) clearly arises between 100 K and 50 K and persists down to 20 K.

As \( \text{Mn}^{2+} \) is substituted into the end member \( \text{ZnMn}_2\text{O}_4 \), ferrimagnetism is induced and can be illustrated by normalizing the FC magnetization using the results of fitting the high-temperature susceptibility to the Curie-Weiss law. The data are then displayed on a common scale, presented in Fig. 7. The utility of such scaling across solid solutions has proven crucial in previous studies of because it offers a clear view of relative strengths of FM/AFM interactions in similar compounds.\(^ {21} \) All samples have Curie temperatures \( \Theta < 0 \text{K} \), indicating that short-range interactions are predominantly antiferromagnetic. The trend of \( \Theta \) versus \( x \) is shown in Fig. 8(a). The strength of antiferromagnetic coupling gradually increases as \( \text{Zn} \) is added to the A-sites, possibly as a consequence of the smaller cell volume as \( \text{Zn}^{2+} \) substitutes \( \text{Mn}^{2+} \). For \( \text{Zn}_x\text{Mn}_{3-x}\text{O}_4 \) samples with \( x < 1 \), these interactions lead to ferrimagnetic order (dropping below the dashed line of ideal Curie-Weiss paramagnetism) with an ordering temperature that decreases with the concentration of tetrahedral \( \text{Zn}^{2+} \).

A more curious trend develops in the paramagnetic effective moment \( \mu_{\text{eff}} \) which is measured above 300 K. In Fig. 8(b), \( \text{Mn}_3\text{O}_4 \) has \( \mu_{\text{eff}} = 8.04 \mu_B/\text{f.u.} \) instead of the ideal value of 9.44 for one tetrahedral \( \text{Mn}^{2+} \) and two
octahedral Mn\(^{3+}\) per formula unit (including both spin and orbital contributions). Interestingly, the experimental \(\mu_{\text{eff}}\) increases with Zn content, despite the removal of \(d\) \(\text{Mn}^{2+}\). If the discrepancy from the ideal value were due to short-range ordering in ZnMn\(_2\)O\(_4\), we would expect lowering of \(\mu_{\text{eff}}\), but this is not the case.

All hysteresis loops measured after ZFC in this system are symmetric around the origin. However, FC loops for \(0 < x < 1\) measured under a cooling field \(H_{\text{FC}} = 50\) kOe are shifted by an exchange bias field \(-H_E\), as seen in Fig.\(\text{[A]}\). Such loop shifts along \(H\) after field cooling are similar to what was first reported by Jacobs and Kouvel.\(^{10}\) A systematic examination of the behavior from \(0 \leq x \leq 1\) reveals an interesting trend. ZnMn\(_2\)O\(_4\) is antiferromagnetic and displays no hysteresis. As \(\text{Mn}^{2+}\) is inserted on the tetrahedral sites, ferrimagnetism arises with a linearly increasing saturation magnetization. In the \(x = 0.25\) and 0.5 samples, the loop shift is exactly equal to the coercivity—that is, \(H_E = H_C\) if we define \(H_C\) to be half the loop width. This implies that for a positive \(H_{\text{FC}}\), nearly all Mn spins that contribute to the ferrimagnetic behavior are pinned in the +\(M\) direction when \(H_{\text{FC}}\) is first relieved. As the hysteresis continues to negative saturation and \(H\) is increased from \(-50\) to \(50\) kOe, there reaches a point where all the Mn ferrimagnetic spins are exactly compensating. This occurs at \(H = 0\). The magnetic saturation \(M_S\) varies smoothly from ZnMn\(_2\)O\(_4\) to Mn\(_3\)O\(_4\), with a contribution of about 0.30(4)\(\mu_B\) per Mn\(^{2+}\), which has \(S = 5/2\) and could contribute a maximum of 5 \(\mu_B\). Because the ferrimagnetic end member Mn\(_3\)O\(_4\) also obeys this relationship, we assume that the inserted Mn\(^{2+}\) create nanoscale clusters of Mn\(_3\)O\(_4\) that are the dominant source of the total magnetic moment. These local FM clusters must be contained within an antiferromagnetic matrix because the exchange bias behavior is genuine, as indicated by the field-cooled loop shifting and centered ZFC loops.

As the tetrahedral Mn\(^{2+}\) fraction increases past 50\%, the loop shift changes from \(H_E = H_C\) to \(H_E = 0\) for the end member Mn\(_3\)O\(_4\). When \(x = 0.75\), \(H_E\) is still present but the positive \(H_C\) value no longer resides at \(H = 0\) as it does for the completely shifted \(x = 0.5\) and 0.25 cases. For a diamond-type lattice such as the A-sites in spinel or heterelite, the site percolation threshold is 43\%.\(^{11}\) As percolation on the tetrahedral sublattice is achieved, loop shifting decreases while \(H_C\) and \(M_S\) vary gradually. So only the dilute spins near edges of clusters are pinned during field cooling, and the pinning is overcome when the clusters grow large or coalesce.

Loop shifts such as those in Fig.\(\text{[A]}\) can arise from two phenomena: classical exchange biasing of a ferromagnet and antiferromagnet, or as a consequence of spin-glass behavior. In the latter case, \(H_{\text{FC}}\) can arise from coupling a ferromagnet to a spin glass,\(^{12}\) glassy uncompensated spins at interfaces/surfaces\(^{13}\) or an intrinsic anisotropy...
FIG. 10: Thermoremanent magnetization (TRM) and isothermal remanent magnetization (IRM) versus applied field for a $x = 0.5$ sample shows clear deviation up to $H = 50$ kOe. Lines are guides to the eye. For a typical spin glass, the two curves should join with increasing $H$ as the field aligns the disordered moments to saturation. In an exchange biased system, the curves remain separated as seen here.

present in the glass itself. One method of testing for spin-glass behavior is the measurement of thermoremanent and isothermal remanent magnetization (TRM and IRM, respectively) shown in Fig. 10. The TRM measurement begins as a typical FC procedure: $H_{FC}$ is applied while cooling from above the magnetic transition, temperature is stabilized, $H_{FC}$ is removed, and the remanent moment $M_R$ is measured. For an IRM measurement, the sample is zero-field cooled, the temperature is stabilized, $H$ is applied for a substantial length of time (here we use 30 min.), the applied field is removed, and $M_R$ is measured. In glassy systems, TRM is greater than IRM for low $H_{FC}$ because additional alignment is induced while cooling through the high-susceptibility glass transition.

At high $H_{FC}$ the values coincide when the applied field overcomes intrinsic anisotropy and aligns all spins, regardless of thermal history. In an exchange biased material, antiferromagnetic spins are not reversed by high fields, so the TRM and IRM curves remain separated even at high fields. Indeed, we can see in Fig. 10 that for $Zn_{0.5}Mn_{2.5}O_4$ high values of $H_{FC}$ produce a higher value for the exchange-biased TRM than the ZFC, non-biased IRM. The TRM/IRM data disallows considering the A-site $\text{Mn}^{2+}$ spins to be a dilute ferromagnetic spin glass that are coupled to an antiferromagnetic B-site sublattice. This measurement further corroborates a two-phase interaction between ferrimagnetic $\text{Mn}_3\text{O}_4$-type clusters with $Zn\text{Mn}_2\text{O}_4$-type antiferromagnetic regions.

Note that these phases are not ordered on the long range, as evidenced most clearly by the diffraction pattern for $Zn_{0.5}Mn_{2.5}O_4$ in Fig. 3(c). The magnetic Bragg peaks disappear when $x = 0.5$, even though the trends in SQUID magnetism continue to vary smoothly. Nevertheless, the ferrimagnetism and exchange bias act as direct interpolations of the $x = 0.25$ and 0.75 samples. In $\text{ZnMn}_2\text{O}_4$ some magnetic ordering produces Bragg peaks, but a loss of Bragg intensity with $x$ signals the breakdown of this B-site ordering from the stronger (but still antiferromagnetic) A-B coupling to the inserted A-site $\text{Mn}^{2+}$.

In the AC magnetization measurements of Fig. 11, two maxima are seen in $\chi'$ under cooling: one at $T_C$ and another at a lower temperature, which is interpreted as a spin-glass freezing $T_f$. The glassy spins may be present at the interfaces between the A-site-induced ferrimagnetic clusters or (less likely) as isolated sites. For samples with $x = 0.75$ and 0.5 (Figs. 11a and 11b), $T_f$ shifts to lower temperatures as the DC bias magnetic field is increased. The $T_f$ versus $H^{2/3}$ dependence plotted in Fig. 11 indicates excellent agreement with de Almeida–Thouless (AT) behavior, which is typical not only for bulk frustrated and dilute spin glasses but also for a wide variety of systems with disordered spins at surfaces and interfaces. No such behavior is seen in the $x = 0.25$ sample, since the Mn spins now occupy 75% of the A-sites and the ferrimagnetic phase has effectively percolated the entire structure. Two key values can be extracted from the AT lines in Fig. 11(d): the freezing tem-
FIG. 12: (Color online) The AC magnetic susceptibility for Zn$_{0.5}$Mn$_{2.5}$O$_4$ exhibits frequency dependence in the region associated with spin glass freezing. The $T$-value of the maximum is plotted versus $f$ in the inset. Error bars are smaller than the data points. The variation of $T_f$ with $f$ agrees with standard spin glass behavior. The $T_g$ extracted from this data differs from that in Fig. 11 due to the large non-glassy ferrimagnetic contribution.

The breadth $T_f$ where irreversibility (hysteresis) in the spin glass is first induced, and the critical field $H_{cr}$ where the applied field overcomes the internal anisotropy of the spin glass and saturates it. Considering Zn$_{0.5}$Mn$_{2.5}$O$_4$, $T_f = 20.6$ K, which is slightly higher than the DC deviation of ZFC-FC data in Fig. 5 as expected since the DC data was collected at $H = 1000$ Oe. More importantly, $H_{cr} = 2020$ Oe. This implies that if the $M_{cr}$ were solely due to a spin glass component the TRM-IRM curves would coincide at $H_{cr}$. As they do not, the number of glassy spins must be very small in comparison to those in ferrimagnetic clusters. Thus the irreversible magnetization in the hysteresis loops of Fig. 9(b) primarily arises from ferrimagnetic regions of local spin alignment and not from glassy clusters that obey AT behavior.

Frequency-dependent AC magnetization measurements of the $T_f$ region in Zn$_{0.5}$Mn$_{2.5}$O$_4$ in Fig. 12 show a deviation after cooling below $T_f$, further evidence of a small amount of glassy behavior. The peak centers are plotted versus $f$ in the inset. The cusp in $\chi'$ obeys the relationship $\Delta T_f/[T_f(\log \omega)] = 0.005$, which is the same value as the canonical spin glass CuMn.\textsuperscript{[10]} The breadth of the peak indicates that there is a distribution of freezing temperatures, based on the non-uniform distribution of glassy spins on interfaces of the ferrimagnetic clusters.

IV. CONCLUSIONS

The system Zn$_x$Mn$_{3-x}$O$_4$ is a homogeneous solid solution when investigated using bulk structural probes such as TOF neutron diffraction. However, magnetic measurements reveal intrinsic exchange bias that we believe results from the interaction of distinct ferrimagnetic and antiferromagnetic regions. For concentrations of Mn-doping up to 50\%, field-cooled hysteresis loops are shifted so that $H_E = H_C$. Because magnetic scattering is diffuse, and the Curie-Weiss temperature $\Theta$ is large and negative, the magnetic structure of the Zn$_x$Mn$_{3-x}$O$_4$ solid solution must consist of ferrimagnetic Mn-rich clusters that do not order on a macroscopic scale. As the clusters grow, their contribution to $M_3$ increases linearly until Mn$_3$O$_4$ is reached, and exchange bias disappears. There is a glassy component to the magnetism in these systems, as evidenced by AC magnetization measurements. However, the contribution of glassy spins to the DC magnetization is minimal, which is most visible in the well-separated TRM and IRM traces even up to large fields. The presence of intrinsic exchange bias merits further investigation of the nanoscale ordering of spins in the Zn$_x$Mn$_{3-x}$O$_4$ system. Small-angle neutron scattering, real-space total scattering, Lorentz transmission electron microscopy, and magnetic force microscopy could each help observe the evolution of magnetic ordering as a function of temperature and composition in this solid solution.

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