Direct Visualization of Magnetic Correlations in Frustrated Spinel ZnFe$_2$O$_4$

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Magnetic materials with the spinel structure (A$^{2+}$B$^{3+}$Zn$^{2+}$Fe$^{3+}$O$_4$) form the core of numerous magnetic devices, and ZnFe$_2$O$_4$ constitutes a peculiar example where the nature of the magnetism is still unresolved. Susceptibility measurements revealed a cusp around $T_C = 13$ K resembling an antiferromagnetic transition, despite the positive Curie–Weiss temperature determined to be $\Theta_{CW} = 102.8(1)$ K. Bifurcation of field-cooled and zero-field-cooled data below $T_C$ in conjunction with a frequency dependence of the peak position and a non-zero imaginary component below $T_C$ shows it is in fact associated with a spin-glass transition. Highly structured magnetic diffuse neutron scattering from single crystals develops between 50 K and 25 K revealing the presence of magnetic disorder which is correlated in nature. Here, the 3D-mPDF method is used to visualize the local magnetic ordering preferences, and ferromagnetic nearest-neighbor and antiferromagnetic third nearest-neighbor correlations are shown to be dominant. Their temperature dependence is extraordinary with some flipping in sign and a strongly varying correlation length. The correlations can be explained by orbital interaction mechanisms for the magnetic pathways and a preferred spin cluster. This study demonstrates the power of the 3D-mPDF method in visualizing complex quantum phenomena thereby providing a way to obtain an atomic-scale understanding of magnetic frustration.

1. Introduction

Ferrites that adopt the spinel structure ($Fd\bar{3}m$, AFe$_2$O$_4$) constitute an important class of magnetic materials,[1] which combine useful magnetic and electronic properties with a high degree of tailor ability through compositional control, particle size, and defects. This versatility has allowed spinel ferrites to find applications not only as magnets but also within many other fields[2] such as microwave devices,[3] catalysis,[4] gas sensing,[5] water purification,[6] and pharmacy.[7]

ZnFe$_2$O$_4$ has been widely studied but considerable disagreement remains about the magnetic nature of the system.[8] Pristine ZnFe$_2$O$_4$ adopts a defect-free normal spinel structure where oxygen forms a distorted cubic closest-packing with Zn$^{2+}$ cations placed at the 8a tetrahedral (A) site and Fe$^{3+}$ at the 16d octahedral (B) site.[9] The unit cell can be constructed from alternating stacking of two building blocks, as shown in Figure 1a–c. Since Zn$^{2+}$ has no magnetic moment the magnetic ions solely reside on the B sites, which constitutes a pyrochlore lattice of corner-sharing tetrahedra (Figure 1d) conducing to magnetic frustration.[10]

Early investigations based on specific heat measurements[11] and neutron powder diffraction[12] suggested that ZnFe$_2$O$_4$ is paramagnetic at room temperature with an antiferromagnetic transition occurring $\approx T_N = 10$ K. However, short-range order has been observed much above the proposed Néel temperature and found to coexist with the long-range order below $T_N$.[13] Usa et al. showed the importance of defects on the magnetism where various treatments to introduce defects induced long-range magnetic order, whereas no sign of such long-range order was found down to 1.5 K in pristine ZnFe$_2$O$_4$ indicating an intrinsically frustrated magnetic system.[14] This was further corroborated by the presence of structured neutron diffuse scattering at low temperatures in ZnFe$_2$O$_4$ single crystals.[15] Theoretical analysis of these diffuse scattering data using an isotropic Heisenberg spin model predicts ferromagnetic nearest-neighbor interaction ($J_1$) and antiferromagnetic third-nearest-neighbor interaction ($J_3$).[16] A ferromagnetic nearest-neighbor coupling is in stark contrast to the earlier descriptions of ZnFe$_2$O$_4$ as an antiferromagnet, but it corroborates the positive Curie–Weiss temperature[15] and excess small angle neutron scattering observed at 89 K.[17] Whether the system constitutes a spin-glass phase below $T_N$ is also debated with susceptibility measurements giving evidence both for[18] and against[19] this interpretation. Despite all the...
evidence for magnetic frustration, a recent report still claims ZnFe$_2$O$_4$ to be an antiferromagnet.\cite{8b} Very recently and during the review process of this manuscript, another paper investigating magnetism in ZnFe$_2$O$_4$ was published. It examines the effect of structural disorder, off-stoichiometry, and inversion on the physical properties and structural parameters.\cite{19} The findings are contrary to those of Usa et al.\cite{14} and it is argued that it is a structural disorder, which gives rise to the magnetic disorder whereas long-range antiferromagnetic order is achieved in perfect crystals, further complicating the picture of the intrinsic properties of this system.\cite{19}

Diffuse scattering arising from magnetic frustration has usually been analyzed using various modeling techniques, but the quality of such results depends on the quality of the initial model and the validity of underlying assumptions, which can lead to model bias and systematic errors. One mean-field method is the classical Heisenberg spin model, as was used by Yamada et al. on ZnFe$_2$O$_4$,\cite{16} where the electrons are assumed to be localized on each site and the Hamiltonian comprised solely of an exchange term. This is a quite simple model which best describes compounds where the magnetic moments of the ions can be adequately described as spin-only. Another example is the development of reverse Monte Carlo methods to model the scattering patterns.\cite{20} Here, a model crystal is constructed and, in the case of magnetic disorder, the magnetic moments rotated individually in a random fashion until the scattering pattern calculated from the model crystal matches the experimental one. This, of course, requires the existence of an ordered atomic structure which can be problematic, especially in materials such as the spinels that can exhibit both structural and magnetic disorder.

Recently, the 3D magnetic difference pair distribution function (3D-mΔPDF) method was developed as a model-free method to directly reconstruct the magnetic correlations from single crystal magnetic diffuse scattering data.\cite{21} The 3D-mΔPDF is the inverse Fourier transform of the unpolarized magnetic diffuse neutron scattering cross-section and is a direct space function with peaks corresponding to interatomic vectors separating more or less magnetization density pointing in the same direction compared to the average periodic structure.\cite{21a} When there is no long-range magnetic order, as is the case for ZnFe$_2$O$_4$, the interpretation becomes comparatively simple; positive (negative) peaks correspond to vectors separating magnetization density pointing in the same (opposite) direction. This method was successfully used to determine the

![Figure 1. The spinel structure. a) The two building blocks of the unit cell with the tetrahedral A block (top) and the octahedral B block (bottom). b) The unit cell built from alternate stacking of the A and B blocks. c) Polyhedral model of the spinel unit cell showing the tetrahedra (green) and octahedra (blue) formed by the distorted cubic closest-packed oxygen (red). d) The corner-sharing tetrahedral network (pyrochlore lattice) formed by the octahedral sites with the tetrahedral arrangement of the third nearest octahedral neighbors highlighted.](https://www.advancedsciencenews.com/doi/abs/10.1002/adma.202301512)
local magnetic correlations in the frustrated spin-glass material bixbyite,[21] despite the simultaneous presence of structural disorder in the form of epitaxial intergrowths and local relaxations in the oxygen sublattice.[22] 

ZnFe$_2$O$_4$ clearly constitutes a delicate magnetic system, where competing orbital interactions between atoms locked in a specific geometrical configuration are easily perturbed. Here we probe the elusive magnetism in ZnFe$_2$O$_4$ using the 3D-$m\Delta$PDF method. Newly synthesized high-quality single crystals (very low cation inversion and no interstitials) were used in the present study (see Supporting Information).

2. Results

2.1. Spin Glass Behavior

Magnetization measurements were performed to investigate the macroscopic magnetic behavior of the ZnFe$_2$O$_4$ single crystals. The static magnetic susceptibility $\chi$ was determined using field-cooled (FC) and zero-field-cooled (ZFC) magnetization (Figure 2a). The ZFC data resembles the expected behavior of an antiferromagnet with a Néel temperature defined by the cusp in the susceptibility at 13.1 K (Figure 2a inset). However, modeling of the temperature dependence of the inverse susceptibility between 260–400 K gives a Curie-Weiss temperature of $\Theta_{CW} = 102.8(1)$ K (Figure 2a inset) indicating that ferromagnetic correlations dominate the spin-spin interactions at room temperature. The large discrepancy between $\Theta_{CW}$ and the apparent transition temperature, $T_c = 13.1$ K, hints at a great degree of frustration, as quantified in the high frustration index $f = |\Theta_{CW}| / T_c = 786(6)$.[23] Furthermore, the bifurcation of the FC and ZFC susceptibility observed below $T_c$ is one of the signatures of a spin-glass transition.[24] The effective moment of the Fe$^{3+}$ ions was calculated from the slope of the Curie–Weiss fit to be $\mu_{eff} = 3.04(5)$ BM, which is only half the spin-only value for high spin Fe$^{3+}$ (5.9 BM) indicating that iron ions do not fit the simple picture of regular octahedral high-spin Fe$^{3+}$.

AC susceptibility measurements were conducted in a frequency range spanning close to four orders of magnitude to further investigate the potential spin-glass transition. The results are displayed in Figure 2b showing a clear shift in the cusp of the real component of the AC susceptibility ($\chi'$) as the frequency increases, another characteristic of a spin-glass transition resulting from its dynamical nature. The peak moves from 13.1 K at 46 Hz to just below 14 K at 9984 Hz (Figure 2b inset), but this frequency dependence is only seen below $T_c$. The peak in $\chi'$ is likewise associated with a sharp maximum in the imaginary component of the AC susceptibility ($\chi''$), which is otherwise zero above $T_c$. Non-zero values of $\chi''$ are related to dissipative processes, such as irreversibility and relaxation processes in the spin-glass phase.[24a,b] Heat capacity measurements confirm the lack of a magnetic phase transition at 13 K (see Supporting Information).

In summary, the physical properties strongly suggest that ZnFe$_2$O$_4$ is a spin-glass and that the cusp in the susceptibility at 13 K is associated with spin-freezing rather than a paramagnetic to antiferromagnetic transition.

2.2. Local Magnetic Correlations

Single crystal neutron scattering was used to gain insights into the apparent magnetic disorder in ZnFe$_2$O$_4$. Neutron diffraction patterns measured at various temperatures between 50 and 1.5 K are shown in Figure 3a–e. Diffuse scattering develops at lower temperatures with highly structured lines appearing between 50 and 25 K signifying that the disorder is locally correlated and not random, which would give only an isotropic diffuse background signal. The lines also decrease in width as the temperature is lowered indicating an increase in the extent of the underlying local correlations.
correlations due to the inverse relationship between the broadness of the diffuse scattering features and the length scale of the local order. \[21b\]

Figure 3f,g show two planes of the isolated diffuse scattering obtained from the 1.5 K dataset highlighting the high degree of structure in the diffuse scattering. The decay in intensity at increasing scattering angle highlights its magnetic, rather than structural, origin since the magnetic form factor decays quite rapidly with scattering angle, as opposed to the nuclear form factor which is nearly constant. 

The local ordering can be elucidated from the sign and position of the peaks in the 3D-m\(\Delta\)PDF combined with knowledge of the atomic structure. Figure 3j–l shows slices in the \(a-b\) plane at three different positions along the \(c\)-axis. The peaks are labeled according to the corresponding atom in (i).

Figure 3. Single crystal neutron scattering and 3d-m\(\Delta\)PDF analysis. a–e) The (hkh) plane reconstructed directly from the raw frames between 1.5 and 50 K showing sharp Bragg peaks from the nuclear structure, powder rings arising from scattering with the sample holder, and broad diffuse scattering in between the Bragg peaks stemming from disorder. As the temperature is lowered the diffuse scattering becomes increasingly structured with more narrow features, indicating that the disorder is correlated rather than random. f,g) Isolated diffuse scattering signal at 1.5 K in two \(hk\) planes of reciprocal space at \(l=0\) (f) and \(l=0.25\) (g) showing its high degree of structure. The decay in intensity at increasing scattering angle highlights its magnetic, rather than structural, origin since the magnetic form factor decays quite rapidly with scattering angle, as opposed to the nuclear form factor which is nearly constant. 

h) The \(a-b\) plane of the 3D-m\(\Delta\)PDF at \(z=0\) Å with clear peaks at short distances indicating the presence of local correlations, while the lack of features further away from the origin highlights that these correlations do not extend far in the structure. i) The octahedral sites in the spinel unit cell (\(a=8.43\) Å) colored according to the sign of the peak of the corresponding interatomic vector in the 3D-m\(\Delta\)PDF (red for a positive correlation and blue for a negative) with respect to the origin atom (0). The number of the labels correspond to the coordination shell relative to atom 0. j–l) A close look at the correlations in the \(a-b\) plane at three different positions along the \(c\)-axis. The peaks are labeled according to the corresponding atom in (i).
is shown with only the octahedral sites. The interpretation of the 3D-mPDF follows from defining one of the sites as the origin (0). Then red and blue atoms tend to have co-parallel and anti-parallel spins compared to 0 respectively. The nearest neighbors (nn1) are all separated by a vector (0, 1/4, 1/4) and its equivalents (a ≈ 8.43 Å). For z = 0 Å and z = 2.11 Å these are clearly seen as positive peaks indicating a preference for co-alignment of neighboring spins. The separation vector to the second (nn2) and third (nn3) nearest neighbors are (1/4, 1/4, 1/2) and (0, 1/2, 1/2) and their equivalents, respectively, and both show up as negative peaks in the 3D-mPDF revealing a preference for antiparallel alignment with nn2 and nn3.

From this analysis, the frustrated nature of the magnetism is apparent; it is not possible to simultaneously have ferromagnetic alignment between nearest neighbors and antiferromagnetic alignment with next-nearest neighbors, only complete ferromagnetic ordering is compatible with co-alignment of all nearest neighbors. In addition, the antiferromagnetic interaction of third nearest neighbors by itself is frustrated since these sites form a face-centered cubic sublattice, an edge-sharing tetrahedral network, which is incompatible with long-range antiferromagnetic order, resulting in multiple levels of frustration being at work in this material. The relative tetrahedral arrangement of the octahedral nn3 atoms is illustrated in Figure 1d.

2.3. Correlations Across the Spin-Glass Transition

The qualitative effect of the temperature on the correlations is shown in Figure 4a–e, where the a–b plane through the origin of the 3D-mPDFs is plotted from 1.5 to 50 K. The increase in correlation length and strength with decreasing temperature is evident, with only weak ferromagnetic nn1 coupling at 50 K evolving into a more complicated picture described above at 1.5 K.

As shown by Roth et al.,[21b] analysis of the integrated 3D-mPDF intensities can give further insights into the spatial and thermal dependence of the correlations. Figure 4f shows the integrated peak intensities for the 20 shortest Fe-Fe distances. The correlation length along any direction can be evaluated by the extent to which significant features exist in the 3D-mPDF. From Figure 4f the correlation length can be estimated at ≈15 Å at 1.5 K, and from the 3D-mPDF itself this appears to be fairly isotropic. Above 17 K there are no strong correlations beyond nn3 at 5.9 Å, but few weak correlations do extend to nn8 at 10.3 Å. This reveals a strong temperature dependence of the correlation length in the vicinity of $T_c$. Interestingly, there are correlations that change sign with increasing temperature (marked by asterisks in Figure 4f). A switch from a ferro- to an antiferromagnetic correlation with changing temperature may suggest competing orbital interactions.

Figure 4. Quantification of magnetic correlations with temperature. a–e) The a–b plane of the 3D-mPDF at z = 0 Å from 1.5–50 K. At 50 K only very weak features are present for the closest neighbors indicating a low degree of correlations between the magnetic moments at this temperature. At 25 K several sets of peaks are present which only grow in intensity as the temperature is further lowered, in addition to peaks showing up at further distances from the origin. This highlights the growth in correlation strength and length as the temperature is lowered. f) The 3D-mPDF integrated peak intensity of the 20 nearest octahedral neighbors as a function of distance for different temperatures (see Supporting Information for details on the integration). The red asterisks mark significant peaks whose sign of correlation depends on the temperature. Some peaks switch signs but only within the light blue region where the change in sign is not sufficiently strong to be considered significant based on the level of noise observed in the 3D-mPDF. g) The intensity of five significant peaks as a function of temperature normalized to their 1.5 K value highlighting the varying temperature dependence of the correlations. h) The top panel shows the intensity ratio of the third and first nearest-neighbor peaks as a function of temperature. The critical temperature, as determined from magnetization measurements, is shown by the blue vertical line. The bottom panel compares the temperature behavior of the sum of the first and third nearest neighbor correlations with that of the second nearest neighbor.
To get a better understanding of the temperature behavior of the individual correlations the normalized intensity of five selected peaks is plotted as a function of temperature in Figure 4g. The rate of decay with temperature varies significantly with the longer correlations generally dying out faster than shorter ones. Comparing for example the 14.6 Å (nn14) peak to the 3.0 Å peak (nn1), the former has dropped more than 90% at 17 K whereas the latter retains more than 70% of its 1.5 K value at this temperature. The temperature dependence of the correlation length is not uncommon in spin glasses but is in clear contrast to the findings for another oxide spin-glass, bixbyite, which showed a nearly constant correlation length with temperature. The varying behavior of the different peaks with temperature corroborates a complex set of competing magnetic interactions in ZnFe$_2$O$_4$.

The integrated intensities reveal that the nn3 correlation is stronger than the nn1 correlation at low temperature: $|nn1|/nn1 = 1.1$ at 1.5 K. The nn3 distance is twice that of the nn1 making this a rather uninteresting result, but it is in line with earlier findings. The top panel of Figure 4h shows the dramatic temperature dependence of the ratio between $|nn3|$ and nn1 with a steep, relatively linear decline from 1.5 to 50 K and then a minor drop up to 150 K. The ratio of 1.1 at 1.5 K is significantly lower than the similar ratio $J_{s}/|J_{d}| = 4.0$ at 1.5 K determined theoretically by Yamada et al. However, the integrated correlation peak intensities are not the same as the $J$-couplings, the former depending on the sum of all magnetic interactions, whereas the latter constitutes the coupling strength of a single exchange pathway, and as such cannot be expected to be identical. The decrease in $|nn3|/nn1$ with temperature is also much more gradual where there is still a significant nn3 contribution at 50 K, compared to Figure 7 in Yamada et al. where $J_{s}/|J_{d}|$ is close to 0 already at 30 K. The bottom panel of Figure 4h shows the striking similarity in the temperature dependence of nn1+nn3 and nn2 alluding to similar underlying mechanisms.

3. Discussion

The estimated $\mu_{eff}$ is significantly lower than the expected spin-only value for Fe$^{3+}$ of 5.9 BM. This has been observed previously, for example, 4.22 BM from neutron powder diffraction refinements or 4.08 BM from Curie-Weiss fitting but not to the extent found here with $\mu_{eff} = 3.04(5)$ BM. Partial covalency of the chemical bonding of Fe$^{3+}$ is a possible explanation for this, as electron sharing would lower the overall moment on the ion. This has been corroborated using ab initio Hartree-Fock cluster calculations, where it was found that the covalency of the Fe–O bond reduced the magnetic moment on Fe$^{3+}$ to 4.2(4). This brings it within the range of the previously found values but fails to account for the even lower value observed here.

Another effect that could lower the magnetic moment is the trigonal distortion of the octahedral site which affects the crystal field splitting of Fe$^{3+}$. This distortion is a result of the oxygen position parameter $u$ deviating from the ideal value of 0.375 (origin at 43m), which corresponds to perfect cubic closest packing. In an octahedral field, the $d$-orbitals split into the lower, triply degenerate $t_{2g}$ orbitals and higher, doubly degenerate $e_{g}$. Upon trigonal distortion the $t_{2g}$ set is further split into an $a_{1g}$ singlet and an $e_{g}$ doublet. If the stabilization of the $a_{1g}$ is sufficiently high it will become favorable for one of the electrons in the $e_{g}$ orbitals to fall into this level making the Fe$^{3+}$ a spin 3/2 ion rather than 5/2, with a corresponding spin-only magnetic moment of 3.87 BM. At higher values of $u$, the octahedra are increasingly distorted resulting in a stronger splitting of the $t_{2g}$ orbitals which potentially leads to Fe$^{3+}$ falling into the spin 3/2 state. Schiessl et al. reported a $u$ value of 0.3845(2) while refinements on single crystal neutron scattering on this batch of ZnFe$_2$O$_4$ crystals gave a value of 0.385119(9) (see Supporting Information). The higher $u$ value seen here, combined with the lower $\mu_{eff}$ could indicate that the splitting is sufficient to affect the Fe$^{3+}$ spin state, where some degree of bond covalency additionally lowers the moment below the expected spin-only value. This strong deviation from the ideal spin 5/2 Fe$^{3+}$ highlights the issues with model-dependent methods, such as the Heisenberg spin model used by Yamada et al. where the simplifications and assumptions of such methods can be at odds with experimental observations. This can result in significant errors or biases in the results.

The magnetic interactions are frustrated at all temperatures, as evidenced by the diffuse scattering occurring significantly above $T_c$. The increase in $|nn3|/nn1$ with decreasing temperature is, in addition to being emblematic of the general increase in correlation length, an indication of a change in the nature of the local spin clusters with temperature. At higher temperatures they are dominated by the shortest-range nn1 interactions which presumably manifest as small ferromagnetic clusters that behave basically independent of each other, as seen from the 3D-mAPDF at 50 K. The weakness of the correlation fails to bring long-range order in the presence of thermal perturbations. As the temperature decreases the relative strength of the antiferromagnetic nn3 correlation increases causing the ferromagnetic spin clusters to preferably align oppositely to neighboring clusters. As nn3 becomes comparable to nn1 the clusters resemble ferromagnetic cores that couple antiferromagnetically to a larger shell. The concurrent increase in correlation strength and length may create an energy barrier that is sufficiently large compared to the thermal energy $k_B T$, and this freezes the spins resulting in the observed spin-glass transition.

The observed magnetic correlations may be understood from the quantum mechanical exchange interactions in the structure. From the 3D-mAPDF intensities, the first- and third-nearest neighbor interactions are the most prominent, in agreement with previous theoretical analysis of single crystal neutron diffuse scattering. The exchange mechanisms in transition metal oxides, such as ZnFe$_2$O$_4$, are often rationalized using the Goodenough-Kanamori-Anderson rules. The different exchange pathways and mechanisms following these rules are discussed below and illustrated in Figure 5.

For nn1 there are two potential pathways: Fe–Fe as a direct exchange $J_1$ and Fe–O–Fe as superexchange through oxygen at a 90° angle $J_2$. The half-filled $d$-shell of Fe$^{3+}$ (electron configuration $[Ar]3d^5$) results in an antiferromagnetic $J_1$, which is weak due to the large overlap distance (Figure 5a), while there are competing ferro- and antiferromagnetic contributions in $J_2$. The ferromagnetic term arises from the
interaction between the Fe 3d eg and O 2p σ orbitals where the orthogonal p-orbitals interacting with each Fe3+ result in a ferromagnetic coupling between the cations (Figure 5b). An example of a potential antiferromagnetic mechanism is the coupling of a 3d eg with a 3d t2g orbital through the same O 2p σ (Figure 5c). The dominating term is, at least partly, dictated by the lattice parameter, where a relative increase of the ferromagnetic term with increasing lattice parameter has been observed in chromite spinels. From the sign of the nn1 peak, it is clear that the total interaction J1 is ferromagnetic revealing that the ferromagnetic J3 is the dominant coupling, resulting in preferential co-alignment of nearest neighbor spins.

The nn2 and nn3 pathways appear identical based on the individual bonds traversed, however, their difference lies in the connections they form to neighboring tetrahedra. Both nn2 and nn3 can be connected via two 90° Fe–O–Fe bonds, that is, the sum of two consecutive J1 interactions. Another possible pathway is through an intermediary tetrahedral Zn, Fe–O–Zn–O–Fe, which also connects to nn2 and nn3, J2 and J3, respectively. A potential exchange mechanism for these pathways is shown in Figure 5d. The Fe 3d eg interacts with the O 2p σ and an orthogonal O 2p-orbital interacts with the empty 4s orbital on Zn2+. The same exchange happens from the other Fe to Zn, however, the electrons virtually transferred from O to Zn must have opposite spins due to the interaction being through the empty 4s orbital of Zn. Thus, the mechanism is identical on either side of Zn, except that all spins are flipped on the right side compared to the left. The net result of these interactions is that the two Fe must have an antiferromagnetic coupling. This agrees with the antiferromagnetic correlation of nn2 and nn3 seen from the sign of the corresponding 3D-mPDF. However, the strength of the correlations differs significantly with the second nearest-neighbor peak being ≈¼ of the third nearest-neighbor peak at 1.5 K (Figure 4f).

The J2 and J3 pathways only differ in the outgoing bond they utilize after the tetrahedral Zn (Figure 5f). Accordingly, the mechanism in Figure 5d is valid for both, and it is thus expected to contribute equally to the nn2 and nn3 correlations. The discrepancy between the observed correlation strength then must lie in other competing interactions, the origin of which is apparent in Figure 5f. J2 connects Fe atoms in adjoining tetrahedra whereas J3 connects atoms in tetrahedra that are not directly connected. The atoms connected by J2 will consequently share a nearest neighbor which will be ferromagnetically coupled to each other creating a competing interaction for nn2. The similar behavior of nn2 and nn1 + nn3 (Figure 4h bottom) reinforces the description of nn2 being governed by a combination of the nn1 and nn3 exchange mechanisms. The downshift in the nn2 curve compared to nn1 + nn3 is expected since the competing ferromagnetic coupling would be through a common nearest neighbor, not a direct one, and the competing ferromagnetic correlation would then be weaker than a pure nn1 interaction.
Figure 5g,h shows two potential preferred spin clusters around any given Fe atom with all nn1, nn2, and nn3 included. Figure 5g is only based on the 3D-mPDF while Figure 5h takes the above considerations on exchange interactions into account. Figure 5g shows the surrounding nn1s are co-aligned giving an hourglass-shaped ferromagnetic core surrounded by a shell of oppositely aligned nn3s, both those connected through Fe–O–Zn–O–Fe (nn3nn) and through Fe–O–Fe–O–Fe (nn3nn) linkages. The oppositely aligned nn2s are disregarded due to their relatively weak correlation strength. In Figure 5h nn3Fe is omitted as these are more likely to be weakly ferromagnetically coupled based on the exchange pathway (a sum of two J1 interactions), and as such are not expected to contribute significantly to the nn3 peaks in the 3D-mPDF compared to those connected through Zn. However, since the nn3Zn and nn3Fe vectors are identical they cannot be distinguished in the 3D-mPDF, a limitation of the method. This magnetic structure is incompatible with the spinel lattice, hence the observed frustration and lack of long-range order. This model is quite different from the dodecamer spin-molecule proposed by Tomiyasu et al.,[30] which has co-alignment of nn3Fe and opposite alignment of nn3Zn.

The present results build on our previous studies on bixbyite which established the 3D-mPDF as a method for investigating magnetic disorder.[21] Those studies highlighted one of the great strengths of the method, namely the ability to reconstruct local magnetic correlations in the presence of structural disorder.[22] Here, we have applied the 3D-mPDF to reveal the magnetic disorder in spinel ferrites, which is not only one of the most important families of magnetic materials, but the contained pyrochlore type lattice is also a major structural motif in studies of spin-frustrated compounds and quantum magnetism. In addition, it was shown that the magnetic correlations extracted from the 3D-mPDF can be used to elucidate the possible underlying exchange mechanisms, moving a step beyond the empirical observations on the correlations presented for bixbyite.

4. Conclusion

The magnetic disorder in ZnFe2O4 has been examined using magnetization measurements along with single crystal neutron diffuse scattering and 3D-mPDF analysis. The static susceptibility showed a cusp at $T_c = 13$ K below which FC-ZFC bifurcation was observed, indicating a transition to a spin-glass phase. A positive Curie-Weiss temperature $\Theta_{CW} = 102.8(1)$ K signified dominant ferromagnetic interactions and considerable magnetic frustration ($\frac{\Theta_{CW}}{T_c} \gg 1$). AC susceptibility revealed a clear frequency dependence of the cusp position in $\chi'$. This, together with a lack of evidence of a magnetic phase transition in the heat capacity data, establishes ZnFe2O4 as a spin-glass material.

Single crystal neutron measurements revealed highly structured diffuse scattering at low temperatures. 3D-mPDF analysis of the diffuse scattering allowed the determination of correlation strengths and signs for the different Fe–Fe nearest neighbors. The magnetic structure is dominated by nearest-neighbor ferromagnetic correlations and third-nearest-neighbor antiferromagnetic correlations. The correlations are very local, with the correlation length peaking at ~15 Å at 1.5 K and decreasing significantly as the temperature is increased. The temperature dependence of individual correlations, as well as the relative magnitudes of the correlations, as exemplified by the strong increase in the [nn3]/nn1 ratio upon cooling below 50 K, suggest competing interactions. The antiferromagnetic nature of the second and third nearest neighbor interactions can be explained from a super-exchange mechanism through the empty 4s orbital of Zn. Analysis of the detailed 3D single crystal neutron diffuse scattering offers a means to build a microscopic understanding of magnetic exchange mechanisms in magnetically disordered materials which is not possible from the Bragg scattering alone.

5. Experimental Section

Single Crystal Growth: ZnFe2O4 single crystals were grown using the flux method. The growth procedure was based on work done by Manzel,[31] who mapped out the part of the solubility curve of Zn and Ni ferrite in PbO. Accordingly, PbO (99.99%, metals basis, Alfa Aesar) was used as the flux material and was mixed with equimolar amounts of Fe2O3 (99.99%, chemPUR) and ZnO (99.99%, metals basis, Alfa Aesar) in a Pt crucible using 50 g of PbO and a 4:1 weight ratio of the flux and the spinel components. The crucible was covered with a loose-fitting lid and partially submerged in Al2O3 sand in a large alumina crucible. The alumina crucible and sand were used as additional thermal mass to mitigate thermal oscillations during the slow cooling to prevent a varying growth rate which would be deleterious to the crystal quality. The alumina crucible was placed in a Nabertherm L5/14 muffle furnace and subjected to the following temperature program: heating to 1473 K at 600 K h−1, then cooling to 1423 K at 10 K h−1 followed by 1 K h−1 cooling down to 1173 K where it was held for 24 h after which the furnace was turned off to cool naturally to room temperature. Once the sample had cooled the PbO was leached with hot HNO3 revealing large, octahedral crystals.

Physical Property Measurements: Heat capacity and magnetization measurements were conducted using a Quantum Design Physical Property Measurement System (PPMS). For the determination of the heat capacity, an addenda measurement was carried out sampling 50 temperatures distributed logarithmically from 1.7 to 300 K to determine the heat capacity of the sample holder. Subsequently, a 16.931(1) mg ZnFe2O4 single crystal was added, and the heat capacity measured at 60 points distributed logarithmically from 1.7 to 300 K. The value at each temperature was taken as the average of three measurements, both for the addenda and sample measurements.

For the magnetization measurements, the PPMS was equipped with an Alternating Current Measurement System (ACMS II) susceptometer. Direct current susceptibility was measured between 1.7 and 400 K at a field strength of 50 Oe. Data was collected continuously upon heating with each data point being a five-second average. From 1.7–10 K the heating rate was 60 K h−1 and above 10 K it was 120 K h−1. The cooling rates were the same in the respective temperature regions. AC susceptibility was measured with a driving field strength of 3 Oe using 10 different frequencies distributed logarithmically between 10 and 10 000 Hz (the two lowest frequencies have been omitted from Figure 2b due to excessive noise). The susceptibility was recorded between 1.7 and 30 K in 1 K increments, except for the region 6–17 K where 74 equidistant data points were collected to get adequate resolution around the cusp.

Neutron Scattering: Single crystal neutron scattering data were collected using two different instruments at the Spallation Neutron Source at Oak Ridge National Laboratory. CORELLI was used to collect elastic diffuse scattering.[32] An octahedral ZnFe2O4 single crystal,
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

frustrated magnetism, magnetic pair distribution function, neutron scattering, spin-glass