Structural change and phase coexistence upon magnetic ordering in the magnetodielectric spinel Mn$_3$O$_4$

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Cooperative Jahn-Teller ordering is well-known to drive the cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ structural distortion in Mn$_3$O$_4$ at 1170$^\circ$C. Further structural distortion occurs in Mn$_3$O$_4$ upon magnetic ordering at 42 K. Employing high-resolution variable-temperature synchrotron x-ray diffraction we show that tetragonal $I4_1/amd$ and orthorhombic $Fd\bar{3}d$ phases coexist, with nearly equal fractions, below the Néel temperature of Mn$_3$O$_4$. Significant variation of the orthorhombic $a$ and $b$ lattice constants from the tetragonal $a$ lattice constant is observed. Structural phase coexistence in Mn$_3$O$_4$ is attributed to large strains due to the lattice mismatch between the tetragonal $I4_1/amd$ and the orthorhombic $Fd\bar{3}d$ phases. Strain tensors determined from Rietveld refinement show a highly strained matrix of the $I4_1/amd$ phase that accommodates the nucleated orthorhombic $Fd\bar{3}d$ phase in the phase coexistence regime. A comparison of the deformation observed in Mn$_3$O$_4$ to structural deformations of other magnetic spinels shows that phase coexistence may be a common theme when structural distortions occur below 50 K.

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I. INTRODUCTION

Phase coexistence is a recurring theme that has been extensively investigated in perovskite manganese oxides displaying colossal magnetoresistance. Phase separation of charge ordered insulating (antiferromagnetic) and metallic (ferromagnetic) phases has been observed in the manganites (La,Pr,Ca)MnO$_3$.[1] Competing double exchange mechanisms and Jahn-Teller-like electron-lattice coupling have been proposed to explain the coexistence of multiple phases.[2,3] Chemical disorder has also been invoked to explain multiscale structural phase separation.[4] However, generalizations in describing the mechanisms of phase coexistence are often insufficient in describing all aspects of these phenomena prompting continued interest in these materials.[5] Here, we encounter structural phase coexistence below the Néel temperature of the spinel Mn$_3$O$_4$.

Mn$_3$O$_4$ (the mineral hausmanite) consists of edge-sharing MnO$_6$ octahedra that are corner connected to MnO$_4$ tetrahedra. It is a cubic spinel in the space group $Fd\bar{3}m$ above 1170$^\circ$C. Mn$_3$O$_4$ undergoes a cooperative Jahn-Teller distortion below 1170$^\circ$C due to orbital degeneracy of the $e_g^1$ states of Mn$^{3+}$ cations that occupy the octahedral sites. Jahn-Teller ordering of the octahedral $e_g$ states stabilizes the $z^2$ orbital by elongating the MnO$_6$ octahedral units resulting in tetragonal $I4_1/amd$ symmetry below 1170$^\circ$C.[6] Mn$_3$O$_4$ is a paramagnet above the Néel temperature ($T_N=41$ K, below $T_N$, it adopts a non-collinear magnetic structure that consists of ferromagnetically coupled Mn$^{2+}$ cations along the (010) direction and two Mn$^{3+}$ sub-lattices with a net moment that couples antiferromagnetically to the magnetization of Mn$^{2+}$ cations. A transition to an incommensurate spiral configuration occurs at 39 K, followed by a transition to commensurate spiral order below 33 K.[7] Commensurate spiral spin ordering in Mn$_3$O$_4$ is described by an orthorhombic magnetic unit cell, which is twice the size of the chemical tetragonal unit cell.[8] Magnon excitations in ferrimagnetic Mn$_3$O$_4$ have been recently investigated by Gleason et al.[9] Magnetism in Mn$_3$O$_4$ couples to its dielectric properties. Consequently, dielectric anomalies are observed near the magnetic transition temperatures. In addition, magnetic field control of the dielectric constant below $T_N$ has also been demonstrated.[10,11,12]

While Jahn-Teller ordering yields a high temperature cubic-tetragonal distortion in Mn$_3$O$_4$,[7] spin ordering drives further lattice distortions in this spinel.[13] Kim et al. reported a transition from tetragonal to monoclinic symmetry in single crystal Mn$_3$O$_4$ at the commensurate spiral ordering temperature ($T\sim33$ K) under zero applied fields.[14] In a subsequent report, Kim and coauthors proposed that the low temperature structure of Mn$_3$O$_4$ is orthorhombic in the space group $Fd\bar{3}d$.[15] Similarly, Chung et al. have recently reported orthorhombic instabilities in Mn$_3$O$_4$.[16] While these initial efforts clearly illustrate a structural transformation in ferrimagnetic Mn$_3$O$_4$, the complete low-temperature structure of Mn$_3$O$_4$ remains unresolved and is the focus of the present work. Extensive studies of the magnetostructural phases of Mn$_3$O$_4$ by Kim and coauthors show that in the presence of large magnetic fields, the structural distortion occurs at higher temperatures in the incommensurate spiral magnetic phase. Remarkably, a spin disordered phase
can be stabilized in Mn$_3$O$_4$ near 0 K when intermediate fields are applied parallel to the (1T0) direction. Here, applied fields transverse to the magnetic ordering direction frustrate spin ordering resulting in disordered spins far below the magnetic ordering temperature. Kim et al. have also shown an increase in the Néel temperature under pressure to temperatures as high as 54 K.

We present here, a complete description of the low-temperature nuclear structure of Mn$_3$O$_4$ finding that tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases coexist in ferrimagnetic Mn$_3$O$_4$. The orthorhombic $Fddd$ phase is spontaneously nucleated at the Néel temperature and its phase fraction increases slightly, attaining a maximum of about 55% near 8 K. The evolution of the unit cell volume as a function of temperature indicates a distortion in both the tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases below 42 K. Distortions in both low temperature tetragonal and orthorhombic phases are corroborated by detailed studies of polyhedra distortions which show deformations in both of these phases. In the orthorhombic phase, MnO$_6$ octahedra show elongation of equatorial Mn-O bonds while the MnO$_4$ tetrahedra show a decrease in the Mn-O bond length. Conversely, the distorted tetragonal phase shows shortened Mn-O equatorial bonds in the MnO$_6$ octahedra and elongated Mn-O bonds in the MnO$_4$ tetrahedra. We examine the role of strain in stabilizing coexisting tetragonal and orthorhombic phases in ferrimagnetic Mn$_3$O$_4$ and make comparisons of the structural distortion of Mn$_3$O$_4$ to those of other magnetic spinels. The complexities in understanding the variations of structural deformations in magnetic spinels are highlighted. The complete structural description of this spinel is pivotal to unraveling the complex ground states of this material. These results necessitate a reinvestigation of the magnetic structure of Mn$_3$O$_4$, which was resolved considering only the tetragonal nuclear structure below the Néel temperature.

II. METHODS

Polycrystalline Mn$_3$O$_4$ was prepared from a MnC$_2$O$_4$·2H$_2$O precursor. The oxalate was decomposed at 600°C for 3 hrs. The precursor powder was then ground, pelletized, and annealed at 1000°C for 24 hrs and water quenched. Variable-temperature (7.5 K–450 K) high-resolution ($\delta Q/\lambda \leq 2 \times 10^{-4}$, $\lambda = 0.41394$ Å) synchrotron x-ray powder diffraction was performed at beamline 11BM of the Advanced Photon Source, Argonne National Laboratory and the ID31 beamline ($\lambda = 0.39985$ Å) of the European Synchrotron Radiation Facility. Variable temperature measurements were collected on heating with a temperature scan rate of 0.8 K/min and an x-ray pattern was collected every 3 minutes. Diffraction patterns were fit to crystallographic models using the EXPGUI/GSAS software program. Crystal structures were visualized using the program VESTA. Density measurements of a powder sample of Mn$_3$O$_4$ were performed on a MicroMetrics AccuPyc II 1340 pycnometer. A sample cup with a volume of 0.1 cm$^3$ was filled with Mn$_3$O$_4$ powder with a mass of 93.1 mg during the density measurement. Temperature-dependent and field-dependent magnetic measurements were performed using the Quantum Design (QD) MPMS 5XL superconducting quantum interference device (SQUID). Heat capacity measurements were collected using a QD Physical Properties measurement system. Mn$_3$O$_4$ pellets for dielectric measurements were spark plasma sintered at 1000°C under a 6 kN load for 3 hrs. Prior to measuring dielectric properties, the spark plasma sintered pellet was annealed at 1000°C for 12 hrs, quenched, and characterized by x-ray diffraction to ensure that stoichiometric Mn$_3$O$_4$ was retained. Dielectric measurements were performed on a pellet with a diameter of 9.51 mm and a thickness of 2.28 mm whose cylindrical faces were coated by conducting epoxy. Dielectric properties were measured by an Andeen-Hagerling AH2700A capacitance bridge connected to the sample by shielded coaxial cables. The sample was placed in a QD Dynacool Physical Properties measurement system which provides a variable temperature and variable field environment when carrying out dielectric measurements.

III. RESULTS AND DISCUSSION

![FIG. 1: (Color online) The room temperature synchrotron diffraction pattern of Mn$_3$O$_4$ modeled using the tetragonal $I4_1/amd$ structure.](image)

At room temperature Mn$_3$O$_4$, is a tetragonal spinel in the space group $I4_1/amd$. The synchrotron x-ray
FIG. 2: (Color online) (a) Temperature dependent magnetic susceptibility measurements of Mn$_3$O$_4$ performed in a 1000 Oe field show a deviation of the zero-field cooled susceptibility from the field cooled susceptibility below the Néel temperature $T_N = 42$ K. (b) Curie-Weiss fitting in the temperature range 500 K $< T <$ 600 K yields an effective moment of 9.02 $\mu_B$ and an expected ordering temperature $|\Theta_{CW}| = 663$ K. High-temperature and low-temperature susceptibility measurements were conducted on different instruments and instrumental variations yield the slight offset between the low-temperature and high-temperature susceptibility that is negligible in plot (a) but emphasized in the $1/\chi$ scaling of plot (b). (c) Field-dependent magnetization shows paramagnetic behavior above the Néel temperature of Mn$_3$O$_4$ and ferrimagnetic behavior below $T_N$ with a saturation magnetization of 1.63 $\mu_B$ and a coercive field of 8.5 kOe when $H = 50$ kOe and $T = 2$ K.

A broad transition from a paramagnetic to a ferrimagnetic state, which is characteristic of polycrystalline Mn$_3$O$_4$, occurs near $T_N = 42$ K. At $T_N$, a separation between the zero-field cooled and field cooled curves develops and is enhanced with decrease in temperature [fig. 2 (a)]. While a single broad magnetic transition is observed in the temperature-dependent susceptibility, the magnetic structure of Mn$_3$O$_4$ is extremely rich, featuring a transition to a collinear magnetic structure at 42 K followed by the onset of an incommensurate magnetic spiral at 39 K, and finally a commensurate spiral magnetic state occurs below 33 K. Each of these transitions is observed in heat capacity and capacitance measurements as discussed later in the manuscript. Curie-Weiss fitting in the temperature range 500 K $< T <$ 600 K yields a $\Theta_{CW}$ of 663 K in good agreement with prior work [fig. 2 (b)]. Comparison between the expected Curie-Weiss ordering temperature and $T_N$ results in a significant frustration index of 15.8. This illustrates that frustration may play a role in the magnetism of Mn$_3$O$_4$. The Curie-Weiss fit also yields an effective moment of 9.02 $\mu_B$ which is congruent with the expected effective moment of 9.11 $\mu_B$ computed from the spin-only effective moments of Mn$^{2+}$ and Mn$^{3+}$ which are 5.92 $\mu_B$ and 4.9 $\mu_B$ respectively. Short-range correlations cause deviations of the inverse susceptibility from the Curie-Weiss model above the Néel temperature as illustrated in fig. 2 (b). The weak linear increase in magnetization with field in the paramagnetic phase evolves to a hysteretic magnetization in ferrimagnetic Mn$_3$O$_4$ [fig. 2 (c)]. A saturation magnetization of 1.63 $\mu_B$ and a coercive field of 8.5 kOe are measured at 50 kOe and 2 K. A collinear ferrimagnetic state in Mn$_3$O$_4$ would yield a saturation magnetization of 3 $\mu_B$/formula unit, however, the measured saturation moment of 1.63 $\mu_B$ is consistent with the reported spiral magnetic structure of Mn$_3$O$_4$ near 2 K. Mn$_3$O$_4$ exhibits significant anisotropy with an easy axis along the (001) direction, which yields a spontaneous magnetiza-
FIG. 4: (Color online) Magnetodielectric coupling in Mn$_3$O$_4$. (a) The dielectric constant as a function of temperature shows three anomalies at 36 K, 39 K, and 45 K which are in close proximity to spin ordering transitions. (b) A magnetic field can modulate the dielectric constant below $T_N$. The changes in the dielectric constant in the presence of a magnetic field increase with decrease in temperature.

Spin ordering in Mn$_3$O$_4$ leads to changes in entropy that are illustrated in fig. 3. Variations in magnetic structure give rise to distinct heat capacity anomalies at 42.5 K, 40 K, and 34.5 K under zero-field conditions. The largest change in entropy occurs at 42 K where the highest heat capacity peak is observed. Entropy changes in Mn$_3$O$_4$ depend on the applied magnetic field, with large fields suppressing the heat capacity transitions. At 10 kOe field, heat capacity peaks are broad but still visible at the transition temperatures and the 42.5 K peak shifts to a higher temperature, $T_N = 43.2$ K. Pronounced suppression of the heat capacity transitions is evident at 50 kOe. The trend in the field-dependent heat capacity reported here, namely, the suppression of heat capacity anomalies and the shift to higher temperatures is in agreement with the work of Kim et al., which reports an increase in $T_N$ in the presence of a field and complete suppression of the onset of magnetic order when a magnetic field is applied along certain crystallographic directions.

Mn$_3$O$_4$ is a known magnetodielectric. Figure 4 (a) shows anomalies in the dielectric constant occurring in close proximity to spin ordering transition temperatures at 45 K, 39 K, and 36 K. The dielectric constant shows no frequency dependence and this illustrates the intrinsic nature of magnetodielectric coupling in the studied Mn$_3$O$_4$ sample. A frequency dependent dielectric constant would indicate that magnetoresistive effects are contributing to magnetodielectric coupling. We also note the presence of dielectric anomalies above 45 K [fig. 4 (a)], which could be linked to short-range spin correlations in the temperature range $T_N < T < |\Theta_{CW}|$. The origin of the dielectric changes above $T_N$ should be further investigated. The dielectric constant exhibits strong field dependence below $T_N$ [fig. 4 (b)]. The field dependence of the dielectric constant increases with decrease in temperature.

The onset of long-range magnetic order in Mn$_3$O$_4$ occurs concurrently with a structural distortion. Figure 5 (a) and (b) show spin and entropy changes occurring concurrently near 42 K. Figure 5 (c) also shows x-ray diffraction evidence of structural changes in Mn$_3$O$_4$ occurring simultaneously near 42 K. A splitting of the tetragonal $I4_1/amd$ (321) reflection to several peaks below 42 K is clearly demonstrated by variable-temperature high-resolution synchrotron x-ray diffraction [Fig. 5 (c)]. The emergence of new diffraction peaks below 42 K indicates...
an average structure distortion. This study of polycrystalline Mn$_3$O$_4$ shows that the magnetostructural distortion occurs near 42 K [fig. 5(c)] while earlier studies of single crystal Mn$_3$O$_4$ have reported a 33 K magnetostructural distortion under zero-field conditions and a 39 K spin-drive structural transition in the presence of an applied magnetic field. The difference in the transition temperature is attributed to varying strain effects in polycrystalline versus single crystal samples; large strains in single crystal samples could suppress the onset of the structural transition. In addition, the cooling and heating rates of the sample during a structural study are also expected to influence the structural distortion temperature.

The precise structural description of Mn$_3$O$_4$ in the ferrimagnetic state is so far unknown. We find that Mn$_3$O$_4$ undergoes a phase transformation from tetragonal $I4_1/amd$ symmetry to a phase coexistence regime consisting of both tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases. Figure 6 (a) shows the 8.2 K diffraction pattern of Mn$_3$O$_4$ modeled by tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases. Structural parameters and goodness of fit parameters obtained from Rietveld refinement are tabulated in Table I. Small goodness of fit parameters along with the agreement between the model and the data illustrates that coexisting tetragonal and orthorhombic phases characterize ferrimagnetic Mn$_3$O$_4$. No single phase low symmetry solution could be obtained to model the low temperature structure of Mn$_3$O$_4$. A closer look at some of the diffraction reflections that split below the Neél temperature is presented in Fig. 6 (b) where the tetragonal (220) reflection coexists with orthorhombic (040) and (400) reflections. Similarly, fig. 6 (c) shows the coexistence of the tetragonal (220) reflection and the orthorhombic (040) and (400) reflections. (c) In a similar way, tetragonal (321) reflection splits giving rise to the orthorhombic $Fddd$ (511) and (151) reflections.

![Image](Image 54x515 to 299x740)

**FIG. 6:** (Color online) (a) The 8.2 K synchrotron x-ray diffraction pattern of Mn$_3$O$_4$ modeled to a structure of coexisting tetragonal $I4_1/amd$ and orthorhombic $Fddd$ structures. (b) The tetragonal $I4_1/amd$ (220) reflection splits giving rise to the orthorhombic $Fddd$ reflections (040) and (400). (c) In a similar way, tetragonal (321) reflection splits giving rise to the orthorhombic $Fddd$ (511) and (151) reflections.

**TABLE I:** Structural parameters of coexisting tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases of Mn$_3$O$_4$ at 8.2 K.

| Temperature (K) | 8.2 |
|----------------|-----|
| Space group    | $I4_1/amd$ |
| Setting        | origin 2 |
| Z              | 4 |
| a(Å)           | 5.75638(1) |
| c(Å)           | 9.44393(4) |
| Vol/(Å$^3$)    | 312.934(1) |
| Mn$^{2+}$      | 4a (0, 1/4, 7/8) |
| Mn$^{3+}$      | 8d (0, 1/2, 1/2) |
| O              | 16h (0, y, z) |
| $U_{iso}$      | 1.41(2) |
| Wt. frac.      | 0.44(6) |
| Space group    | $Fddd$ |
| Setting        | origin 2 |
| Z              | 8 |
| a(Å)           | 8.11602(5) |
| b(Å)           | 8.16717(5) |
| c(Å)           | 9.44209(5) |
| Vol/(Å$^3$)    | 625.869(4) |
| Mn$^{2+}$      | 8a (1/8, 1/8, 1/8) |
| Mn$^{3+}$      | 16d (1/2, 1/2, 1/2) |
| O              | 32h (x, y, z) |
| $U_{iso}$      | 1.38(1) |
| Wt. frac.      | 0.4869(2) |
| z              | 0.2585(2) |
| Mn$^{2+}$      | 1.25(2) |
| Mn$^{3+}$      | 1.21(2) |
| O $U_{iso}$    | 1.45(3) |
| Wt. frac.      | 0.50(6) |
| $\chi^2$      | 3.206 |
| $R_p(\%)$      | 5.46 |
| $R_{wp}(\%)$   | 6.82 |
cent report from our group shows structural phase coexistence in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$.

The low-temperature structures coexist with nearly equal fractions below $T_N$. Weight fractions of 50.4% and 49.6% for the $I4_1/amd$ and $Fddd$ phases respectively are measured near $T_N$. With decrease in temperature below $T_N$, the orthorhombic phase fraction increases slightly attaining a maximum value of 56% near 8 K. Scherrer analysis reveals that large crystallite sizes with dimensions >10μm are observed in the high temperature and low temperature tetragonal phases while smaller domain sizes of about 690 nm characterize the orthorhombic phase. The simple Scherrer model of crystallite size analysis neglects instrumental broadening, therefore, the sizes obtained are the minimum values.

At the magnetostructural ordering temperature of Mn$_3$O$_4$, orthorhombic $Fddd$ lattice constants emerge and coexist with tetragonal $I4_1/amd$ lattice constants (Fig. 7). The orthorhombic $a$ and $b$ lattice constants derive from the tetragonal $a$ lattice parameter. $A \approx 0.3\%$ compression of the orthorhombic $a$ axis and $a \approx 0.33\%$ elongation of the orthorhombic $b$ axis relative to the tetragonal $a$ lattice constant are measured [Fig. 7 (a)]. The continuous decrease of the tetragonal $c$ axis that occurs above 42 K, is disrupted at $T_N$ where the orthorhombic $c$ axis emerges with values $\approx 0.02\%$ smaller relative to the tetragonal $c$ axis [Fig. 7 (b)]. The temperature-dependence of the unit cell volume shows a discontinuous decrease below 42 K [Fig. 7 (c)]. In the Ehrenfest classification of phase transitions, first order phase transitions are characterized by a discontinuous change in the first derivative of the free energy. The discontinuous change in the cell volume of Mn$_3$O$_4$ and coexistence of two low-temperature structures suggests that this is a first order phase transition. The structural distortion of Mn$_3$O$_4$, $b_{\text{orth}}/a_{\text{tet}} = 1.003$, is of the same order as those of other spin driven lattice distortions observed in the related spinel compounds NiCr$_2$O$_4$, CuCr$_2$O$_4$, ZnCr$_2$O$_4$, and MgCr$_2$O$_4$.

The complete crystallographic description of Mn$_3$O$_4$ enables detailed investigation of polyhedral distortions that occur following the structural distortion. The elongated MnO$_6$ polyhedral units of tetragonal Mn$_3$O$_4$ above $T_N$ are described by an apical bond length of 2.275(9) Å, which is twofold degenerate and an equatorial bond length of 1.93(3) Å that is fourfold degenerate [Fig. 8 (a) and (b)]. Below the structural transition temperature, the apical bond length remains fairly temperature-dependent of the structural parameters of Mn$_3$O$_4$. (a) Variation of the tetragonal $a$ lattice constant of Mn$_3$O$_4$ with temperature shows the emergence of a compressed orthorhombic $a$ lattice constant and an elongated orthorhombic $b$ lattice constants below 42 K. (b) The tetragonal $c$ lattice constant decreases with temperature to 42 K, below which the orthorhombic $c$ lattice constant, which has a decreased value, emerges. (c) A linear decrease in the unit cell volume is observed above 42 K. At 42 K, a discontinuous decrease in cell volume is observed in both the tetragonal $I4_1/amd$ and orthorhombic $Fddd$ phases.
perature independent with small variations around the 2.275(5) Å value in both the tetragonal and orthorhombic phases[Fig. 8(a)]. On the other hand, below $T_N$, the equatorial bond length of the tetragonal phase decreases to a length of about 1.92(5) Å while retaining its fourfold degeneracy. The equatorial Mn-O bond length of MnO$_6$ octahedra exhibits distortions in the orthorhombic phase that yield two Mn-O bond lengths that are about 1.935(5) Å long, each with twofold degeneracy [Fig. 8(b)]. The high temperature tetragonal phase has a tetrahedral Mn-O bond length of 2.04 Å, this bond length increases to $\approx 2.05(3)$ Å in the low temperature tetragonal phase while it decreases in the orthorhombic phase to $\approx 2.025(4)$ Å [Fig. 8(c)]. The distortions of the polyhedra in each of the low temperature structures are complementary, for instance examining the low temperature orthorhombic phase: the elongation of the equatorial bond lengths of MnO$_6$ octahedra are compensated by the decrease in Mn-O bond lengths of the MnO$_4$ tetrahedra.

High resolution synchrotron x-ray diffraction has emerged as an important tool for characterizing the low temperature structures of magnetic materials. However, it has been shown that chemical inhomogeneity that is present at all times, but cannot be easily detected by high resolution x-ray diffraction above the phase transition temperature, can lead to structural phase coexistence below a structural phase transition temperature. In this light, we have refined the elemental occupancies of all atoms in the low temperature tetragonal and orthorhombic phases. All elements remain stoichiometric within error. The highest vacancy concentration of 1.33% is obtained for Mn$^{3+}$ cations in the orthorhombic phase. Nevertheless, this small vacancy concentration cannot account for >50% orthorhombic phase content observed below $T_N$. We have performed high-precision density measurements of the Mn$_3$O$_4$ sample to further investigate the stoichiometry of this material. Density measurements of the powder sample at room temperature give a density of 4.855(9) g/cm$^3$ which compares well with the expected density of 4.86 g/cm$^3$ confirming that off-stoichiometric effects are not influencing the structural phase transition of this sample.

Structural phase coexistence in Mn$_3$O$_4$ is linked to large strains at the phase transition temperature due to the lattice mismatch between the low temperature orthorhombic phase and the high temperature tetragonal phase. Figure. 7 shows that the orthorhombic $a$ and $b$ lattice constants vary by 0.3% from those of both the high temperature and low temperature tetragonal phases. The $c$ axis varies slightly, by 0.02% between the $Fddd$ and $I4_1/amd$ phases. The map of the strain tensor shows a highly strained low temperature tetragonal phase (Fig. 9). Most of the strain is along the crystallographic $a$ and $b$ axes where the largest lattice mismatch between the low temperature tetragonal and orthorhombic phases is observed. The orthorhombic $Fddd$ phase also experiences slightly higher strain compared to the high temperature tetragonal phase. It is important to note the significantly smaller strain along the [001] direction, this finding agrees well with the fairly invariant $c$ lattice constants of the high temperature and low temperature phases. Evidence of strain stabilized structural phase coexistence in Mn$_3$O$_4$ is corroborated by the work of Suzuki and Katsufuji, who have performed strain measurements on single crystals of Mn$_3$O$_4$ observing changes in the temperature dependent strain ($\Delta L/L$) at the magnetic ordering temperatures. Suzuki and Katsufuji also show larger strain effects along the [110] plane of Mn$_3$O$_4$ compared to the [001] direction.

Evidence of coexisting tetragonal and orthorhombic phases is in agreement with prior studies of the hausmanite Mn$_3$O$_4$. Chung et al. reported orthorhombic instabilities in a single crystal of Mn$_3$O$_4$ after observing subtle diffraction peak asymmetry. The study by Chung et al. essentially indicates the present of coexisting phases in

![Image](54x93.png)

FIG. 9: (Color online) Ellipsoid representation of the second rank strain tensor of Mn$_3$O$_4$ in the various phases as determined by Rietveld refinement using the Pseudo-Voigt with Finger-Cox-Jephcoat asymmetry(GSAS profile 3) profile function. In addition to the color scale, the size of the ellipsoid scales with the magnitude of the strain. In all the phases of Mn$_3$O$_4$, large strains are observed in the [110] plane compared to the [001] direction. The low temperature tetragonal $I4_1/amd$ phase is highly strained compared to the high temperature tetragonal phase and low temperature orthorhombic phase. The high temperature $I4_1/amd$ phase shows the lowest strains of the three phases of Mn$_3$O$_4$.

| Microstrain term | 298 K $I4_1/amd$ | 8.2 K $I4_1/amd$ | 8.2 K $Fddd$ |
|------------------|------------------|------------------|------------------|
| $L_{11}$         | 0.1071           | −0.0257          | 0.1666           |
| $L_{22}$         | 0.159            | −0.3624          | 0.1975           |
| $L_{33}$         | 0.0743           | 0.1071           | 0.0837           |
| $L_{12}$         | 0.1093           | 0.3676           | −0.0481          |
| $L_{13}$         | −0.0151          | −0.0392          | −0.0127          |
| $L_{23}$         | −0.0218          | −0.02115         | −0.0350          |

TABLE II: Microstrain terms of the various phases of Mn$_3$O$_4$ obtained from Rietveld refinement. The magnitude of the microstrain terms of the low temperature tetragonal phase are larger than those of the other phases of Mn$_3$O$_4$. These strain tensors have been plotted in an ellipsoidal representation in Fig. 9. Pseudo-Voigt profile with Finger-Cox-Jephcoat asymmetry was employed in describing the diffraction lineshapes.
Mn$_3$O$_4$ below $T_N$, with the tetragonal phase yielding dominant peaks and the orthorhombic phase contributing to mere peak asymmetry. Considering the work of Chung and coworkers, it is clear that large strains in a single crystal can inhibit the formation of a large phase fraction of the low temperature orthorhombic phase. The polycrystalline sample examined here along with the use of high-resolution synchrotron x-ray diffraction allows us to fully resolve the diffraction reflections of the orthorhombic $Fddd$ phase and to complete a detailed study of the structural changes taking place at low temperatures.

The structural phase transformation of Mn$_3$O$_4$ bears some of the hallmark characteristics of a martensitic phase transformation. We observe the nucleation of an orthorhombic $Fddd$ phase within the matrix of the parent $I4_1/amd$ phase. Strain energy inhibits the complete structural transformation of Mn$_3$O$_4$ to the orthorhombic phase, stabilizing a mixed phase structure. Comparable strain-mediated structural phase coexistence is reported in the manganites Bi$_{0.2}$Ca$_{0.8}$MnO$_3$ and La$_{0.275}$Pr$_{0.35}$Ca$_{0.375}$MnO$_3$. However, it must be noted that the pervoskites are usually on the verge of being metals and the inhomogeneities are frequently the result of very slightly differing levels of chemical doping, but this is not the case in Mn$_3$O$_4$ because it is stoichiometric and insulating. Examination of hysteresis effects of the structural phase transition of Mn$_3$O$_4$ are inconclusive due to slow heating and cooling rates applied during variable temperature x-ray measurements. A comparison of the magnetostuctural phase transformation of Mn$_3$O$_4$ to spin-driven lattice deformations of other magnetic spinels suggests that phase coexistence likely occurs when structural deformations occur at low temperatures ($T < 50$ K) (Fig. 10). However, the spind GeCo$_2$O$_4$ shows a full transformation from cubic to tetragonal symmetry near 22 K indicating that low temperatures do not necessarily limit full structural transformations in all spinels and perhaps the particular strains involved in the lattice deformation play a larger role in stabilizing phase coexistence.

These results call for a re-examination of the properties of Mn$_3$O$_4$ at low temperatures. For example, how do we understand spin ordering in the various low temperature phases? Further, it is important to resolve the magnetic structure of Mn$_3$O$_4$ taking into account structural phase coexistence in the ferrimagnetic phase. Since strain influences phase coexistence, it presents a new approach to controlling the magetostructural phase transition of Mn$_3$O$_4$ to achieve a desired low temperature structure.

![Table of phase coexistence](image)

| Compounds        | Phase Coexistence       |
|------------------|-------------------------|
| CuCr$_2$O$_4$    | Fddd, I4$_1$/amd, Fd-3m |
| NiCr$_2$O$_4$    | Fddd, I4$_1$/amd, Fd-3m |
| MnMnO$_4$ (Mn$_3$O$_4$) | Fddd + I4$_1$/amd, Fd-3m |
| GeCo$_2$O$_4$    | Fddd + I4$_1$/amd, Fd-3m |
| MgCr$_2$O$_4$    | Fddd + I4$_1$/amd, Fd-3m |
| ZnCr$_2$O$_4$    | Fddd + I4$_1$/amd, Fd-3m |

FIG. 10: (Color online) Structural distortions in some spinels due to Jahn-Teller ordering and magnetostructural coupling effects. While in many instances full structural transformations occur, phase coexistence is observed for MgCr$_2$O$_4$, ZnCr$_2$O$_4$, and Mn$_3$O$_4$.

IV. CONCLUSIONS

High resolution synchrotron x-ray diffraction reveals the coexistence of tetragonal $I4_1/amd$ and orthorhombic $Fddd$ below the Néel temperature of the magnetodielectric spinel Mn$_3$O$_4$. The two low temperature phases coexist in nearly equal fractions. A complete crystallographic description of Mn$_3$O$_4$ in the ferrimagnetic state is presented. Polyhedral distortions in the ferrimagnetic phase of Mn$_3$O$_4$ are described. We show that strains due to the lattice mismatch between the orthorhombic phase, which is nucleated below 42 K, and the high temperature tetragonal $I4_1/amd$ phase likely contribute to the observed phase coexistence. We propose strain as a new approach to control the properties of Mn$_3$O$_4$ below the magnetic ordering temperature.

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