Mapping the magneto-structural quantum phases of Mn$_3$O$_4$

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We present temperature-dependent x-ray diffraction and temperature- and field-dependent Raman scattering studies of single crystal Mn$_3$O$_4$, which reveal the novel magnetostructural phases that evolve in the spinels due to the interplay between strong spin-orbital coupling, geometric frustration, and applied magnetic field. We observe a structural transition from tetragonal to monoclinic structures at the commensurate magnetic transition at T$_2$=33K, show that the onset and nature of this structural transition can be controlled with an applied magnetic field, and find evidence for a field-tuned quantum phase transition to a tetragonal incommensurate or spin glass phase.

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Strong coupling among the spin, lattice, and orbital degrees of freedom in the geometrically frustrated spinel compounds [1] results in a rich variety of exotic magnetic and structural phases and properties that are of both scientific and technological interest. For example, the chromium-oxide spinels AB$_2$O$_4$ (A=Zn, Cd, Hg; B=Cr) exhibit three-dimensional spin-Peierls transitions involving coupled magnetic and structural transitions:[2-6] the vanadium-oxide spinels AB$_2$O$_4$ (A=Zn, Cd, Mn; B=V) display complex spin/orbital ordering and technologically useful phenomena such as large magnetoelastic and magnetodielectric effects;[7-14] and sulfer-based spinels such as FeB$_2$S$_4$ (B=Cr,Sc) [15] exhibit orbital-liquid or -glass ground states in which frustration prevents orbital ordering down to T=0. The rich magnetostructural phases of the spinels are thought to be governed by the interplay between spin-orbital coupling, applied magnetic field, and frustrated exchange interactions,[1,16] but there has been little experimental investigation of the microscopic details of this interplay.

The binary spinel Mn$_3$O$_4$ is a relatively simple system for experimentally studying the complex interplay between structure, spin-orbital coupling, and magnetic field in the spinels: in spite of its simpler chemical composition—with Mn ions at both tetrahedral (A=Mn$^{2+}$) and octahedral (B=Mn$^{3+}$) sites—Mn$_3$O$_4$ exhibits the rich magneto-structural transitions characteristic of more complex ternary magnetic spinels: Below T$_C$=43K, the spins in Mn$_3$O$_4$ exhibit Yafet-Kittel-type ferrimagnetic ordering, in which the net spin of the octahedrally coordinated Mn$^{3+}$ spins is antiparallel to the [110] direction of the tetrahedrally coordinated Mn$^{2+}$ spins, with pairs of Mn$^{3+}$ spins canted by $\pm \theta_{YK}$ from the [T10] direction, where $\cos \theta_{YK}=0.38$ (0.33) at T=4.7K and $\cos \theta_{YK}=0.40$ (0.25) at T=29K for the “non-doubling” octahedral (“doubling” octahedral) site.[14,17] However, below T$_1=39K$, Mn$_3$O$_4$ develops an incommensurate sinusoidial or spiral spin structure of the Mn$^{3+}$ spins; and below T$_2=33K$, Mn$_3$O$_4$ exhibits a commensurate spin structure in which the magnetic unit cell doubles the chemical unit cell.[17,18] Recent studies also show that the magnetic transitions in Mn$_3$O$_4$ are associated with significant temperature- and field-dependent changes in the dielectric constant and lattice parameters, reflecting strong spin-lattice coupling in this material.[19,20]

In this paper, we report Raman spectroscopy and x-ray diffraction measurements of the temperature- and magnetic-field-dependent phases of single-crystal Mn$_3$O$_4$. These combined measurements offer a particularly clear, microscopic view of the diverse magnetostructural phases that can result from the interplay between strong spin-orbital coupling, geometric frustration, and applied magnetic field in the spinels; this includes evidence for a quantum phase transition to a tetragonal spin/orbital glass phase for intermediate fields with H||[110], which we propose is caused by a field-tuned degeneracy between magneto-structural states.

A single-crystal sample of Mn$_3$O$_4$ was grown at the University of Illinois using a floating zone technique; the sample was identified as a single phase crystal using both x-ray powder diffraction with a Rigaku D-Max system and a pole figure analysis with a Phillips X’pert system. Field-dependent Raman measurements were performed as described previously [21] on an as-grown surface of single crystal Mn$_3$O$_4$ having a surface normal along the [110] direction. Temperature-dependent x-ray measurements were carried out using a Rigaku rotaflex RU-300 with a closed-cycle He refrigerator in the range of 10K to 75K. In addition, a Phillips MRD X’Pert was used for high precision measurements at room temperature. Both measurements were performed on the as-grown [110] surface of single crystal Mn$_3$O$_4$. A least squares program was used to determine the lattice parameters of the crystal from the data.

The room-temperature Raman spectrum of our Mn$_3$O$_4$ sample exhibits 5 phonon peaks, consistent with previous reports:[22] a T$_{2g}$ symmetry mode at 290 cm$^{-1}$, an E$_g$ symmetry mode at 320 cm$^{-1}$, T$_{2g}$ symmetry modes at 375 cm$^{-1}$ and 479 cm$^{-1}$, and an A$_{1g}$ symmetry mode
FIG. 1: (a) Illustrations of the monoclinic structure for T<T2=33K and the tetragonal structure of Mn3O4 for T>T2=33K. (b) Contour plot of the T2g phonon mode intensity as functions of energy and increasing temperature, where red=700 counts and blue=0 counts. (inset) Contour plot of the T2g phonon mode intensity over the full temperature range 7-290K. (c) Temperature dependence of γ—the angle between the a- and b-axis directions—as functions of increasing temperature (closed symbols) and decreasing temperature (open symbols). (inset) Temperature dependence [in K] of lattice constants a (squares), b (triangles), and c (circles) [in Å] for Mn3O4. Open (closed) symbols represent measurements taken with decreasing (increasing) temperature.

at 660 cm⁻¹.[22,23] In this paper, we focus on the lowest energy T2g phonon mode, which is associated with Mn-O bond-stretching vibrations of the tetrahedral sites.[22,23]

Fig. 1(b) shows the temperature dependence of the T2g mode intensity and the T2g mode energy and linewidth for light polarized along the [110] crystallographic direction of Mn3O4. Three distinct temperature regimes can be identified: (i) T>T1=39K – Above T1=39K, the T2g mode narrows and shifts to higher frequencies with decreasing temperature in a conventional manner, i.e., consistent with a temperature dependence governed by anharmonic (multi-phonon) effects.[24] (ii) T2=33K<T≤T1=39K – In the incommensurate magnetic phase regime between T2=33 K and T1=39K, the lowest T2g mode decreases in energy slightly with decreasing temperature due to magnetoelastic effects, but exhibits no evidence for a change in structural symmetry. (iii) T<T2=33K – Below the commensurate magnetic transition T2=33K, the T2g mode abruptly splits into three modes near 290 cm⁻¹, 295 cm⁻¹, and 300 cm⁻¹. This splitting is consistent with a tetragonal-to-monoclinic distortion below T2, which splits the degenerate T2g mode by expanding the Mn²⁺-O²⁻ bond length along the easy-axis [110] direction and contracting the Mn²⁺-O²⁻ bond length along the hard-axis [110] direction (see illustrations, Fig. 1(a)). Note that the relative intensities of the three modes shown in Fig. 1(b) for T<T2 confirm that the Mn²⁺-O²⁻ bond length expands along the easy-axis [110] direction below T2=33K: the higher-energy (~300 cm⁻¹) split mode—which is associated with vibrations of the contracted Mn²⁺-O²⁻ bond—exhibits the strongest light scattering intensity, indicating that the contracted Mn²⁺-O²⁻ bond is oriented in the direction of the incident light polarization, i.e., along the [110] direction. By contrast, the intensity of the lower-energy (~290 cm⁻¹) split mode—which is associated with vibrations of the expanded Mn²⁺-O²⁻ bond—has a substantially weaker intensity than the ~300 cm⁻¹ mode, consistent with an expansion of the Mn²⁺-O²⁻ bond in a direction perpendicular to the incident light polarization, i.e., along the [110] direction.

To provide more definitive evidence for a tetragonal-to-monoclinic phase transition below T2 in Mn3O4, temperature-dependent x-ray diffraction measurements were performed on the same crystal. Fig. 1(c) shows the temperature dependence of the lattice parameters a, b, c, and γ—the angle between a and b—as functions of both increasing (“warming”) and decreasing (“cooling”) temperature. While γ exhibits an abrupt decrease near T2=33K—indicating an abrupt decrease in the angle between a- and b-axis directions at this temperature, the lattice parameters a and b exhibit no significant temperature dependence, and the lattice parameter c exhibits only a weak temperature dependence and hysteretic behavior. This behavior confirms that Mn3O4 exhibits a first-order tetragonal-to-monoclinic structural phase transition near T2=33K, as illustrated schematically in Fig. 1(a). Notably, the observed monoclinic crystal structure we observe below T2=33K is consistent with the spin structure that has been previously reported for Mn3O4 below T2: the coplanar spin structure of the doubled unit cell has spins lying within the (110) plane, without a net spin along [110], in which the Mn³⁺ spins are cantied by an angle ±θ/4K from the [110] direction. This spin canting is associated with a tilting of the d₃z²-r² orbitals of Mn³⁺ toward the [110] direction due to spin-orbital coupling, which results in a tilting of Mn³⁺ octahedra and an expansion of the Mn²⁺-O²⁻ bond length along the [110] direction.[17,20] We also note that the monoclinic structure we observe for the incommensurate magnetic phase regime between T2=33K and T1=39K...
FIG. 2: (a) Field dependence of the Raman spectra at T=39K for H∥[110]. (b) Illustrations of the Mn$_3$O$_4$ structure in (top) the low-field undistorted phase and (bottom) the high-field monoclinic phase. (c) Contour plots of the intensities of the split modes as functions of energy and field at (left) T=34K, (middle) 39K, and (right) 44K, where red=700 counts and blue=0 counts for H∥[110]. (d) Phase diagram as functions of magnetic field (along [110]) and temperature; orange region=structure I, yellow region=structure II, IC=incommensurate magnetic phase, C=commensurate (cell-doubled) magnetic phase.

(Fig. 1(b)) is consistent with the presence of an axially symmetric spiral spin structure [17] in this temperature regime.

The distinctive Raman spectroscopic signatures associated with the different magneto-structural phases in Mn$_3$O$_4$—illustrated in Fig. 1(b)—offer a convenient method for investigating the phases induced with an applied magnetic field. Fig. 2 illustrates the field-induced structural phases of Mn$_3$O$_4$ for fields applied along the easy-axis [110] direction. Fig. 2(a) and the left and middle plots of Fig. 2(c) show that, in the incommensurate magnetic phase regime $T_2=33K < T \leq T_1=39K$, the $\sim 295\text{cm}^{-1}$ mode associated with the undistorted tetragonal phase (structure II in Fig. 2(b)) exhibits a field-induced splitting similar to that induced upon cooling below $T_2=33K$ in zero magnetic field (Fig. 1(b)). Thus, in the incommensurate magnetic phase, an applied magnetic field along the easy axis [110] direction induces a tetragonal-to-monoclinic distortion in Mn$_3$O$_4$ by forcing the Mn$^{3+}$ spins to order within the (110) plane and inducing the cell-doubled coplanar magnetic structure associated with the monoclinic structure (see Fig. 2(b)). This strong magnetoelastic response at rather modest fields likely arises from a field-induced increase—via spin-orbit coupling—in the hybridization between the $d_{3z^2-r^2}$ and $d_{xy}$ orbitals of Mn$^{3+}$ for H∥[110], and demonstrates that the magnetostructural states I and II in Fig. 2(b) have
very similar free energies. Fig. 2(d) summarizes the differ-
ent magnetic/structural phases of Mn$_3$O$_4$ as functions of
magnetic field and temperature for H∥[110].

A richer magneto-structural phase diagram is observed
when the magnetic field is applied along the hard-axis [110] direc-
tion (structure I) persists at low fields. On the other
hand, at high magnetic fields, i.e., for H > 4T for T=7K,
Figs. 3(a) and (c) show that the low-energy 290cm$^{-1}$
mode is most intense, indicating a monoclinic phase in
which the field reorients the Mn spin—and expands the
Mn$^{2+}$-$O^{2-}$ bond length along the easy-axis [110] di-
rection (structure III).

Most remarkably, however, Figs. 3(a) and (c) show
that the field-induced transition from a monoclinic dis-
tortion with M∥[110] to a monoclinic distortion with
M∥[110] is not abrupt, but occurs via an intermediate
field regime (1T < H < 4T) in which the dominant mode is the
$\sim$295cm$^{-1}$ mode, i.e., the mode associated with
the undistorted tetragonal phase (structure II in Figs. 3(b)
and 3(c)) observed in the paramagnetic and incommensu-
rate phases above $T_2=33K$ for H=0 (Fig. 1(b)). We sug-
gest that the quantum phase transition to this intermediate
phase is a transition from a ferrimagnetic, monoclinic
phase with M∥[110], to a “spin/orbital” glass phase—in
which the Mn spins are randomly oriented along the [110]
and [110] directions—or to an incommensurate spiral spin
phase; both of these possibilities are consistent with a
tetragonal structure (see Fig. 1(b)). Fig. 3(c) shows
that, with increasing temperatures, this field-induced
tetragonal regime becomes more pronounced. Fig. 3(d)
summarizes the different magnetic/structural phases of
Mn$_3$O$_4$ as functions of magnetic field and temperature
for H∥[110].

The results summarized in Fig. 3(d) indicate that
the competition between spin-orbital coupling, geomet-
rical frustration, and applied magnetic field in Mn$_3$O$_4$
leads to an incommensurate—or even glassy—spin state
at T=0 that is sandwiched—as a function of applied field
with H∥[110]—between commensurate spin phases. The
observation of a quantum phase transition to an inter-
mediate incommensurate or spin-glass tetragonal phase
(structure II in Fig. 3(b))—rather than a simple metam-
agnetic transition between or coexistence of commensu-
rate ferrimagnetic phases (structures I and III in Fig.
3(b)) at intermediate fields—likely reflects the impor-
tance of spin-lattice coupling in Mn$_3$O$_4$, wherein the bal-
ancing of elastic and magnetic energies favors the forma-
tion of a more isotropic magnetostructural configuration at
intermediate fields with H∥[110]. Indeed, this more
isotropic magnetostructural configuration (II) appears to
be the means by which Mn$_3$O$_4$ resolves the frustra-
tion that arises from the field-induced degeneracy between
M∥[110] and M∥[110] spin configurations at intermediate
field values with H∥[110]. Field-dependent neutron scat-
tering and heat capacity measurements would be useful
for clarifying the nature of the spin configuration and
entropy of this highly frustrated field-induced state. It
is also important to study the T→0 spin dynamics of
this intermediate-field isotropic phase, in particular to
explore the extent to which quantum critical fluctuations
govern the dynamics in this frustrated phase regime.

In summary, combined temperature- and field-
dependent Raman scattering and temperature-
dependent x-ray scattering studies provide a clear
microscopic view of the diverse and complex magne-
tostructural phases that evolve in the spinel material
Mn$_3$O$_4$ due to the interplay between spin-orbital cou-
ing, geometrical frustration, and applied magnetic
field. In addition to identifying the specific structural
phases associated with the different magnetic states
observed in Mn$_3$O$_4$ with H=0, we have identified the
microscopic magnetostructural changes that are
associated with the novel magnetodielectric behavior
previously observed for this material. Most interesting
is the observation of a quantum phase transition to
a structurally isotropic, incommensurate/disordered
spin state for intermediate fields with H∥[110], which
reflects a compromise this system takes to accommodate
the frustration imposed by a field-induced degeneracy
between differing magnetostructural states.

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