Stability of the ferromagnetic ground state of La$_2$MnNiO$_6$ against large compressive stress

D. Haskel,[1,*] G. Fabbris,[1,2] N. M. Souza-Neto,[3] M. van Veenendaal,[1,4] G. Shen,[5] A. E. Smith,[6] and M. A. Subramanian[6]

[1]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Department of Physics, Washington University, St. Louis, Missouri 63130, USA*
[3]*Laboratorio Nacional de Luz Sincrotron-LNLS, Campinas, Sao Paulo, Brazil*
[4]*Department of Physics, Northern Illinois University, De Kalb, Illinois 60115, USA*
[5]*HPCAT, Carnegie Institution of Washington, Argonne, Illinois 60439, USA*
[6]*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003, USA*

The effect of quasi-hydrostatic pressure upon the ferromagnetic ground state of magnetodielectric, double-perovskite La$_2$MnNiO$_6$ is investigated using x-ray absorption spectroscopy and diffraction measurements in a diamond anvil cell. The Mn-O-Ni superexchange interaction that gives rise to ferromagnetism in this cation-ordered structure is stable to at least 38 GPa (380 000 atm). Such unusual stability of a ferromagnetic state to applied pressure can be rationalized in terms of the electronic and crystal structure and should help preserve the outstanding electronic and magnetic properties of this material when grown epitaxially under moderate compressive and tensile strain conditions.

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The ferromagnetic-insulating character of double-perovskite La$_2$MnNiO$_6$, together with a Curie temperature ($T_c \sim 280$ K) near room temperature,[1] magnetodielectric response,[2] and demonstrated pulsed laser deposition (PLD) growth of epitaxial films,[3] has generated significant interest for potential applications of this material in spin-based electronics. While most transition-metal (TM) monoxides with sodium chloride structure are antiferromagnetic (AFM) insulators due to a negative superexchange (SE) interaction between divalent TM ions,[4] distorted double-perovskite La$_2$MnNiO$_6$ orders ferromagnetically (FM) due to a positive SE interaction between Mn and Ni cations. The sign of superexchange coupling depends both on the degree of cation order and the oxidation state (3d orbital occupancies) of Mn and Ni cations.[5] While a high degree of cation order is well established,[6] both (Mn^{4+},Ni^{2+}) (Ref. 7) and (Mn^{3+},Ni^{3+}) (Ref. 6) valence states have been reported. In addition, the stability of the ferromagnetic ground state against applied pressure (compressive stress), to the best of our knowledge, has not been studied. Pressure studies not only help understand the nature of the FM state but also can be used as predictors of the magnetic properties in epitaxial thin films grown under compressive (tensile) strain on selected substrates.[3] In particular, whether the magnetic ordering temperature can be enhanced past room temperature with the application of pressure/stress is worth exploring.

To this end we have undertaken x-ray absorption and diffraction studies on polycrystalline samples of La$_2$MnNiO$_6$. Samples were prepared from starting metal nitrate solutions using solid-state synthesis as described in Ref. 2. X-ray absorption near-edge structure (XANES) and magnetic circular dichroism (XMCD) measurements at the La $L_{2,3}$ and Mn,Ni K edges were carried out at beamline 4-ID-D while powder x-ray diffraction (XRD) was measured at the HPCAT beamline 16-BM-D, both at the Advanced Photon Source, Argonne National Laboratory.

Figure 1 shows XANES data for both Mn and Ni K edges in La$_2$MnNiO$_6$, together with reference oxide compounds with a known valence state. The threshold for K-edge absorption

(1s core electron excitation), determined from the centroid of the leading absorption edge, is very sensitive to the oxidation state[8,9] and direct comparison with the reference compounds yields Mn^{4+} and Ni^{2+} valence states. This validates the conclusions in Ref. 7 and is at odds with the 3+ oxidation state for Mn and Ni ions deduced from structural data in Ref. 6. The SE coupling between tetravalent Mn ($t_{2g}^3 e_g^0$, $S = 3/2$) and divalent Ni ($t_{2g}^6 e_g^2$, $S = 1$) cations mediated by oxygen anions is ferromagnetic,[5] as illustrated in the top panel of Fig. 1. Note that Mn^{4+}-O-Mn^{4+} and Ni^{2+}-O-Ni^{2+} bonding resulting from cation disorder would lead to AFM-SE interactions[5] (Fig. 1). The robust FM state observed in La$_2$MnNiO$_6$ (Ref. 2) is a testament to the high degree of cation ordering, as directly determined by neutron diffraction.[6]

Magnetization data confirms FM alignment of Mn and Ni moments, although the saturation moment in our sample (4.5μ_B/f.u. at 5 K) is reduced from a purely ionic model (5μ_B/f.u.). Such reduction is usually a result of some degree of covalency in interatomic bonding, although imperfect cation ordering may also contribute.[6] Indeed, density functional theory (DFT)[10] finds 2.6/1.4μ_B at Mn/Ni sites, 0.1μ_B at oxygen sites, and a small La 5d moment of 0.022μ_B. We probed element-specific magnetism with XMCD. Measurements were carried out in helicity-switching mode (13.3 Hz) and the accuracy of XMCD signals was verified by consecutive measurements in opposite applied fields ($H = 0.8$ T). XMCD confirms the FM coupling of Ni and Mn magnetic moments (Fig. 2). Although we observe a sizable XMCD signal ($\sim 1\%$) at La $L_{2,3}$ edges (Fig. 2) as a result of induced exchange splitting in the La 5d states, a sum rule analysis[11] yields a small La 5d moment of 0.026(6)μ_B [$m_s = 0.022(6)\mu_B, m_l = 0.004(2)\mu_B$]. The lack of a spin-moment sum rule for the K-edge XMCD spectra prevents us from unambiguously determining the relative orientation of the induced La 5d moment. However, DFT predicts a FM coupling with (Mn,Ni) moments.[10] The induced nature of La 5d exchange splitting is also seen in the coupled temperature-dependent XMCD signals at La L_2 and Mn,Ni K edges (Fig. 2).
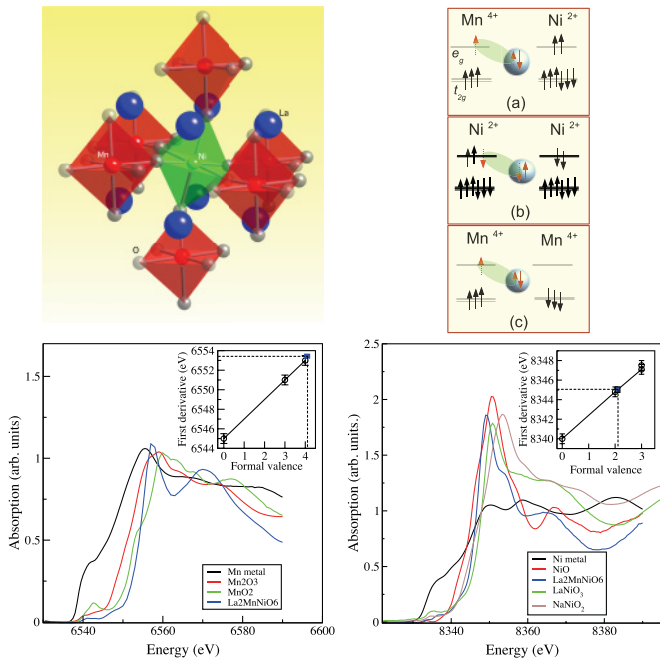
FIG. 1. (Color online) (Top left) Crystal structure of La_2MnNiO_6. Mn (red, left) and Ni (green, center) cations occupy centers of corner-sharing oxygen octahedra. (Top right) Schematic representation of SE interactions in cation-ordered (a) vs cation-disordered (b), (c) FM and AFM structures, respectively. (Bottom) Mn (left) and Ni (right) K-edge XANES spectra in La_2MnNiO_6 and reference compounds.
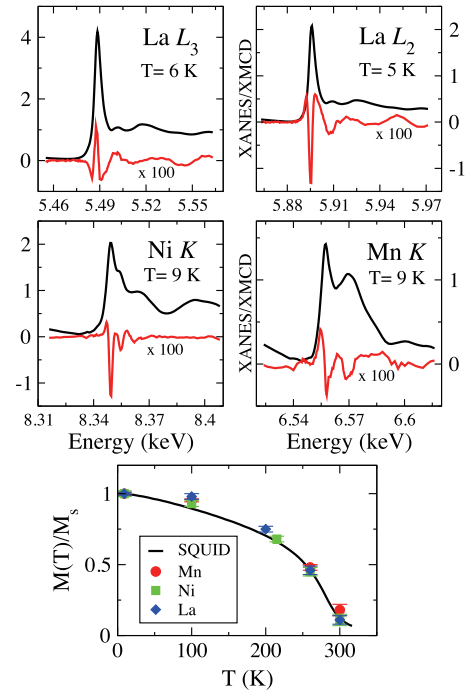

FIG. 2. (Color online) Normalized La $L_{2,3}$ edge (top panel) and (Ni, Mn) K edge (middle panel) XANES and XMCD data measured at ambient pressure in a $H = 0.8$ T field. Bottom panel: Temperature-dependent SQUID magnetization data and integrated XMCD intensities.

XMCD measurements in the diamond anvil cell (DAC) were used to check the stability of the FM state against applied pressure. A membrane-driven, copper-beryllium DAC with perforated diamond anvils was used for high-pressure XMCD measurements at the Ni K edge (8.345 keV). The DAC mounts on the cold finger of a liquid helium (LHe) flow cryostat placed between the pole pieces of an electromagnet, delivering 0.48 T at the sample.[12] Powders of La_2MnNiO_6 were loaded into the 120-μm hole of a rhenium gasket preindented to 45 μm, together with silicon oil as pressure-transmitting medium and ruby spheres for *in situ* pressure calibration at all temperatures. The culet size of diamonds was 300 μm. Figure 3 shows temperature-dependent (normalized) magnetization data collected at ambient pressure [superconducting quantum interference device (SQUID) magnetometry] and under applied pressures (Ni K-edge XMCD). We observe no measurable change in saturation magnetization or Curie temperature within errors to the highest measured pressure of 38 GPa. To rule out that an anomalously low compressibility could be responsible for such a remarkable stability of the FM ground state, we directly measured the pressure dependence of the unit-cell volume using high-pressure XRD measurements. These measurements use a symmetric DAC with conical seats and the same diamond culet size and gasket parameters used in the XMCD measurements, albeit with neon as the pressure-transmitting medium and Au as the pressure calibrant. High-pressure XRD patterns were collected at 200 K between 1.6 and 50 GPa. Lattice parameters were refined within the rhombohedral *R-3* space group[6] and the bulk modulus was determined by fitting the measured pressure-volume

relationship to a third-order Birch-Murnaghan equation of state,[13] yielding $B_0 = 188(28)$ GPa, $B_0' = 4(1)$ (Fig. 4). This is comparable to the bulk modulus of steel (160 GPa) and falls in between that of NiO (190 GPa) (Ref. 14) and MnO (150 GPa).[15] While possessing strength like steel makes this material attractive for applications under extreme stress conditions, the compressibility is comparable to that of other oxides and hence is not unusually low. No evidence for pressure-induced valence transitions is found in either the XANES (Fig. 3) or compressibility (Fig. 4) data.

While in direct-exchange ferromagnetic metals[16] or itinerantlike ferromagnetic oxides[17] applied pressure suppresses magnetic ordering through band broadening and a related decrease in electron-electron correlations from the outset, the situation is different in SE (insulating) oxides, where magnetism is mediated by the overlap of the spin-carrying electron's wave function with that of nominally nonmagnetic oxygen ions. In the absence of structural distortions this SE interaction is expected to *increase* with pressure. However, preservation of the ambient pressure magnetic ground state does not necessarily take place, e.g., as a result of competing FM and AFM SE interactions,[18] crystal-field-driven spin transitions,[19] or hybridization,[20] all of which can largely impact the nature and degree of magnetic ordering, as well as the saturation magnetization. In the case of La_2MnNiO_6, a number of factors contribute to the stability of the FM ground state. Given the Mn^{4+} and Ni^{2+} oxidation state of the cations and their ordering, competing AFM interactions are not present and would only come into play if the Ni-O-Mn bond angle gets closer to 90° than 180° (Ref. 5) (this angle is ~160° at
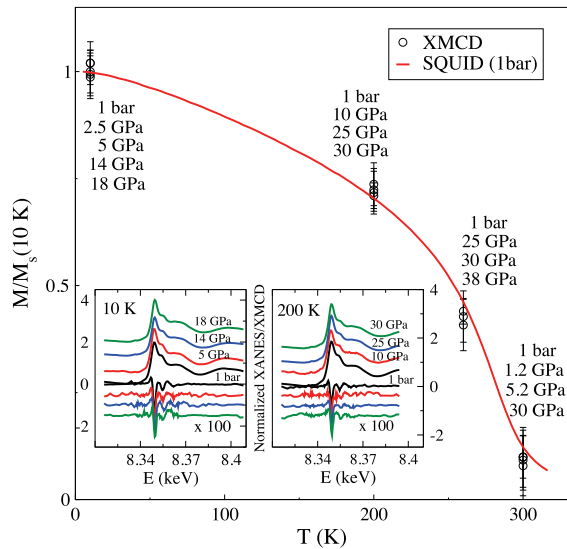
FIG. 3. (Color online) Pressure dependence of Ni K-edge XMCD intensity at various temperatures, together with SQUID magnetization data (main panel). XANES data (insets) show the absence of valence transitions within this pressure range.

$P = 1$ bar[2]), or if cation ordering is destroyed, neither of which occurs under the measured pressure and temperature conditions. Furthermore, a crystal-field-driven spin transition would require at minimum a lifting of degeneracy in Mn t_{2g} or Ni e_g states. Such a transition is not observed within the measured pressure range, indicating preservation of nearly octahedral (O_h) local symmetry or a Hund coupling's stabilization of Mn and Ni high-spin states up to the highest measured pressure. [For example AFM-NiO (MnO) is known to retain its high-spin state to at least 100 GPa (40 GPa).[21]]

In order to understand the absence of a measurable increase in magnetic ordering temperature we turn to theoretical calculations. As noted above, the strength of the FM superexchange interaction J is expected to increase under pressure. Estimates of J generally give a t_{pd}^4 dependence,[22,23] where t_{pd} is the hopping integral between the transition-metal and the oxygen ligand. From 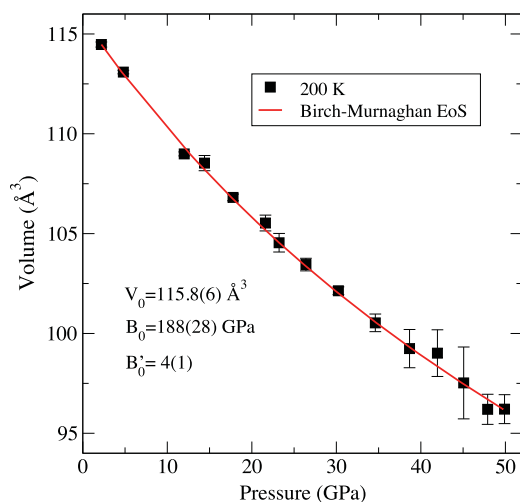density functional theory,[24] it is known that the hopping integral scales as $r^{-3.5}$, where r is the metal-ligand distance. From the volume change (Fig. 4), we can estimate a lattice parameter reduction of $\sim$4% at 40 GPa. This implies an increase in J of $\sim$77%. Since the critical temperature is directly proportional to J, such an increase clearly contradicts the experimental findings. In order to obtain a better estimate of the change in the nearest-neighbor exchange interaction as a function of pressure, calculations were done using a Ni-O-Mn cluster in the manner described in Ref. 25. Coulomb interactions, including full multiplet effects, were taken into account. The monopole part of the interaction was 6 eV for both Mn and Ni sites, and a crystal field $10Dq = 1.5, 2.5$ eV was used for Ni and Mn sites, respectively. The hybridization parameters between the transition metals and oxygen were $(pd\sigma) = 1.3$ eV and $(pd\pi) = -0.45(pd\sigma)$. The hybridization was included assuming octahedral symmetry so that no lowering of symmetry occurs. The charge-transfer energies $\Delta_{Ni/Mn}$ for La_2MnNiO_6 are not well known. The superexchange interaction couples the nickel ($S_1 = 1$) and manganese ($S_2 = 3/2$) spins, giving states with a total spin of $S_{tot} = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. For an interaction $-J\mathbf{S}_1 \cdot \mathbf{S}_2$, the eigenenergies are $-\frac{3}{2}J, J, \frac{5}{2}J$, respectively. Although the cluster cannot be perfectly mapped onto a spin-spin interaction, the lowest eigenstates are split in this fashion within 5%, allowing for a determination of J. When taking $\Delta_{Ni} = 4$ eV and $\Delta_{Mn} = 2.5$ eV, we find $J = 33$ meV. What is more important for our considerations is the change in J as a function of pressure. We include a 4% decrease in the lattice parameter by adjusting t_{pd} and $10Dq$ according to the $r^{-3.5}$ and r^{-5} power laws.[24] This increases J to 35 meV. Note that this is an increase of only 7%, which is significantly less than the 77% expected from perturbation theory. It should be noted that the crystal field and hybridization counteract each other. Including only hybridization gives an increase in J of 17%, whereas inclusion of only the change in the crystal field leads to a decrease in J of 10%. However, both changes are still significantly less than expected from the perturbation result.

A possible reduction in the Mn-O-Ni bond buckling angle under pressure would further reduce the increase in J. The effective hopping parameter scales as $\cos(90° - \theta/2)/\cos(90° - \theta_0/2)$, where $\theta_0 \sim 160°$ is the buckling angle at ambient pressure.[26] Although we lack information on how the buckling angles change under pressure, a reduction in buckling angle from 160° to 140° would reduce the increase in J to only 1.7% under a 4% reduction in lattice parameter. The corresponding change in magnetic ordering temperature would fall within our experimental errors. It follows that the ferromagnetic ground state is stable to 38 GPa, but competing hybridization and crystal-field interactions, together with (possible) buckling distortions, prevent a significant increase in magnetic ordering temperature from taking place.

In summary, ferromagnetic-insulator and magnetodielectric La_2MnNiO_6 displays a remarkable stability of the FM state against large compressive stress, adding to an already impressive list of remarkable properties. This stability is not a result of an unusually small compressibility, but rather is due to the absence of competing AFM interactions and spin transitions in the measured pressure range, dictated by the unique cation ordering, $3d$ electron occupancies at TM sites, and Hund's coupling stabilization of their high-spin states. Our

FIG. 4. (Color online) Pressure-volume relationship at $T = 200$ K measured with powder XRD.

results imply that PLD films grown epitaxially under moderate (a few percent) compressive or tensile strain are likely to retain their saturation magnetization and ordering temperature. This indeed appears to be the case,[3] although data on fully strained PLD films is yet to become available. A compressibility like steel and a saturation magnetization comparable to that of Ni metal make this ferromagnetic material attractive for usage in extreme stress environments.

*haskel@aps.anl.gov

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