The ferromagnetic-insulating character of double-perovskite La$_2$MnNiO$_6$, together with a Curie temperature ($T_C \sim 280$ K) near room temperature, 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.

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

D. Haskel, G. Fabbris, N. M. Souza-Neto, M. van Veenendaal, G. Shen, A. E. Smith, and M. A. Subramanian

Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

Department of Physics, Washington University, St. Louis, Missouri 63130, USA

Laboratorio Nacional de Luz Sincrotron-LNLS, Campinas, Sao Paulo, Brazil

Department of Physics, Northern Illinois University, De Kalb, Illinois 60115, USA

HPCAT, Carnegie Institution of Washington, Argonne, Illinois 60439, USA

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003, USA

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The ferromagnetic ground state of La$_2$MnNiO$_6$, together with reference oxide compounds with known valence state. The threshold for a known valence state. The threshold for a known valence state.

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. Magnetization data confirms FM alignment of Mn and Ni moments, although the saturation moment in our sample (4.5$\mu_B$/f.u. at 5 K) is reduced from a purely ionic model (5$\mu_B$/f.u.). Such reduction is usually a result of some degree of covalency in interatomic bonding, although imperfect cation ordering may also contribute. Indeed, density functional theory (DFT) finds 2.6/1.4$\mu_B$ at Mn/Ni sites, 0.1$\mu_B$ at oxygen sites, and a small La 5$d$ moment of 0.022$\mu_B$. We probed element-specific magnetism with XMC. Measurements were carried out in helicity-switching mode (13.3 Hz) and the accuracy of XMC signals was verified by consecutive measurements in opposite applied fields ($H = 0.8$ T). XMC confirms the FM coupling of Ni and Mn magnetic moments (Fig. 2). Although we observe a sizable XMC signal (~1%) at La $L_2$ edge (Fig. 2) as a result of induced exchange splitting in the La 5$d$ states, a sum rule analysis yields a small La 5$d$ moment of 0.026(6)$\mu_B$ [$m_L = 0.022(6)\mu_B, m_T = 0.004(2)\mu_B$]. 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 5$d$ moment. However, DFT predicts a FM coupling with (Mn,Ni) moments. The induced nature of La 5$d$ exchange splitting is also seen in the coupled temperature-dependent XMCD signals at La $L_2$ and Mn,Ni $K$ edges (Fig. 2).
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. Powders of $\text{La}_2\text{MnNiO}_6$ 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 and the bulk modulus was determined by fitting the measured pressure-volume relationship to a third-order Birch-Murnaghan equation of state, 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) and MnO (150 GPa). 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 or itinerant-like ferromagnetic oxides 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, crystal-field-driven spin transitions, or hybridization, all of which can largely impact the nature and degree of magnetic ordering, as well as the saturation magnetization. In the case of $\text{La}_2\text{MnNiO}_6$, 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 $\sim 160°$ at...
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 \(t_{pd}\) 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 10\(D_q\) = 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 \((pd\pi) = -0.45\, (pd\pi)\). 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 \( -JS_1\cdot S_2\), the eigenenergies are \(\pm\sqrt{\frac{1}{2}}, J, \pm\sqrt{3J}, J\), 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 10\(D_q\) 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 \(\cos(90^\circ - \theta)/\cos(90^\circ - \theta_0)/2\), where \(\theta_0 \sim 160^\circ\) 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\(^\circ\) to 140\(^\circ\) 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, 3\(d\) electron occupancies at TM sites, and Hund’s coupling stabilization of their high-spin states. Our
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, 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.

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