Perovskite-type manganites have recently received renewed interest after the observation of a “colossal” negative magnetoresistance (CMR) effect in La$_{1-x}$Ca$_x$MnO$_3$ [1] and related materials. Correlated magnetic and metal-insulator transitions are observed as a function of temperature, magnetic field, and doping along with charge and orbital ordering/disordering phenomena (for recent reviews, see [2,3]). The complex electronic properties of doped manganites originate from an intimate interplay of lattice and electronic degrees of freedom. This is also the case for the undoped parent compound, LaMnO$_3$. At ambient conditions LaMnO$_3$ is an insulator with orthorhombic perovskite structure (space group $Pnma$ [4]). Alternating long and short Mn-O2 distances in the $ac$ plane of the structure are a sign of orbital ordering which arises from a cooperative Jahn-Teller (JT) distortion. The latter removes the degeneracy of the $e_g$ orbitals in the $t_{2g}^3e_g^1$ electron configuration of the Mn$^{3+}$ ions and stabilizes the 3$d_{3z^2-r^2}$ with respect to the 3$d_{x^2-y^2}$ orbitals. It is the origin of $A$-type antiferromagnetism below $T_N \approx 140$ K [5].

There has been intense discussion about the primary cause of the insulating ground state of LaMnO$_3$ (see, for example, Refs. [6,7]). In one interpretation LaMnO$_3$ is regarded, like many insulating transition-metal oxides, as a Mott-type (or charge-transfer) insulator, i.e., the electrical properties are dominated by electron-electron interactions leading to a localization of the $e_g$ conduction electrons. On the other hand, Millis et al. concluded that the insulating behavior of the paramagnetic phase cannot be explained by a purely electronic model [6]. Strong Jahn-Teller electron-phonon coupling was proposed as the crucial component which localizes the $e_g$ electrons as polarons.

High pressure is a means to tune the interplay between lattice and electronic degrees of freedom in LaMnO$_3$. We have studied the effect of hydrostatic pressure on the structural, vibrational, optical, and electronic properties of LaMnO$_3$ by angle-dispersive synchrotron x-ray powder diffraction, Raman spectroscopy, optical reflectivity, and electrical resistance measurements. Our data reveal that the cooperative Jahn-Teller distortion of LaMnO$_3$ is continuously reduced with increasing pressure. The JT effect and the concomitant orbital order are completely suppressed above 18 GPa. The system, however, retains its insulating state to $\sim$32 GPa, where it undergoes a bandwidth-driven insulator-metal transition. Delocalization of electron states, which suppresses the JT effect but is insufficient to make the system metallic, appears to be a key feature of LaMnO$_3$ at 20–30 GPa.

LaMnO$_3$ was studied by synchrotron x-ray diffraction, optical spectroscopies, and transport measurements under pressures up to 40 GPa. The cooperative Jahn-Teller (JT) distortion is continuously reduced with increasing pressure. There is strong indication that the JT effect and the concomitant orbital order are completely suppressed above 18 GPa. The system, however, retains its insulating state to $\sim$32 GPa, where it undergoes a bandwidth-driven insulator-metal transition. Delocalization of electron states, which suppresses the JT effect but is insufficient to make the system metallic, appears to be a key feature of LaMnO$_3$ at 20–30 GPa.

LaMnO$_3$ was prepared from a stoichiometric mixture of La$_2$O$_3$ and Mn$_2$O$_3$ which was prefired in air at 1300 °C, pressed into pellets, and fired again at 1300 °C. Finally, the sample was heated at 700 °C in a gas flow containing 95% Ar and 5% H$_2$. The lattice parameters and Mn-O distances of our sample at ambient conditions are in good agreement with the values reported for stoichiometric LaMnO$_{3.00}$ [4].

The structural properties of LaMnO$_3$ under pressure were studied up to 40 GPa by monochromatic ($\lambda$ = 45.09 pm) x-ray powder diffraction at the European Synchrotron Radiation Facility (ESRF Grenoble, beam line ID9). Diffraction patterns were recorded on image plates and then integrated [8] to yield intensity vs. $2\theta$ diagrams. A diamond anvil cell (DAC) was used for pressure generation with nitrogen as a pressure medium to provide nearly hydrostatic conditions. Raman spectra of LaMnO$_3$ up to 16 GPa (DAC, methanol/ethanol pressure medium) were recorded using an Ar-ion laser (515 nm) and a triple-grating spectrometer with a CCD detector. Optical reflectivity spectra of LaMnO$_3$ in the energy range 0.6–4.0 eV were measured at pressures up to 38 GPa using...
a micro-optical setup and sample loading procedures (KCl pressure medium) described in Ref. [9]. All of the above experiments were performed at $T = 300$ K. Four-probe dc resistance measurements were carried out with 5–7 $\mu$m thick Pt foil electrodes as a function of temperature and pressure [10]. The sample/metal-gasket cavity was coated with an insulating mixture of Al$_2$O$_3$/NaCl combined with epoxy. No pressure-transmitting medium was used. In all experiments pressures were measured with the ruby luminescence method [11].

Typical diffraction patterns of LaMnO$_3$ are shown in Fig. 1(a) for the pressure range 0–40 GPa. Up to 11 GPa the diffraction patterns were suitable for Rietveld refinements [12] yielding the lattice parameters and the atomic positions. Figure 1(b) shows the result of a refinement for a pressure of 5.9 GPa. Above 11 GPa, lattice parameters were determined from full-profile fits with the atomic positions fixed to the 11-GPa values (space group $Pnma$).

Figure 2(a) illustrates the pressure dependence of the lattice parameters. The $b$-axis data are normalized by a factor of $2^{-1/2}$ corresponding to a pseudocubic representation of the lattice. Up to 15–20 GPa, the compression is anisotropic with the soft direction along the $a$ axis. Its initial compressibility is $\sim 4$ times larger than those of the $b$ and $c$ axes. The compressibilities along the $c$ and $a$ directions change markedly at $\sim 7$ and $\sim 18$ GPa, respectively. LaMnO$_3$ remains orthorhombic to at least 40 GPa.

From the lattice parameter data we obtain the pressure dependence of the unit-cell volume shown in Fig. 2(b). The $V(P)$ data are well described by the Murnaghan equation [13] which yields the bulk modulus $B_0$ and its pressure derivative $B'_0$ at zero pressure. The large value of $B'_0 = 8.5 \pm 0.4$ (compared to typical values of $B'_0 = 4$–6 for crystals with nearly isotropic compression) reflects the pronounced anisotropic compressibility.

![Figure 1](image1)

**FIG. 1.** (a) X-ray powder diffraction patterns of LaMnO$_3$ at various pressures ($T = 298$ K). (b) Diffraction pattern at 5.9 GPa and difference between the observed and calculated profile. Marks show the calculated peak positions. The reflection marked “$N_2$” is due to solid nitrogen.

Figure 2(c) shows the free positional parameters $x$ and $z$ of the La ions as a function of pressure. The $x$ parameter decreases continuously and becomes zero near 12 GPa. This is also evidenced directly by the decreasing intensity of the (111) reflection [cf. Fig. 1 and inset of Fig. 2(c)]. The fact that this reflection does not reappear at higher pressures implies that the La ions remain located at $x = 0$ (and $x = 1/2$) at pressures above 12 GPa. The structural data further indicate that the relative compression of the distorted MnO$_6$ octahedra is larger than that of the unit cell [inset in Fig. 2(b)]. This implies that the octahedral tilting decreases with increasing pressure, consistent with the shift of the La ion. Mizokawa et al. concluded that at ambient pressure the shift of the La ion, driven by the GdFeO$_3$-type distortion, is essential to stabilize the orbital ordering [14]. The observed reversal of this shift thus suggests a destabilization of the orbital order at high pressures.

The three Mn-O distances of the distorted MnO$_6$ octahedra decrease under pressure [Fig. 2(d)]. This effect is most

![Figure 2](image2)

**FIG. 2.** (a) Lattice parameters of LaMnO$_3$ at ambient temperature as a function of pressure. There are marked changes of the $a$ and $c$ axis compressibility at 7 and 18 GPa, respectively. The inset shows the crystal structure of LaMnO$_3$ at ambient conditions (space group $Pnma$). (b) Unit-cell volume versus pressure. The inset depicts the volume of the MnO$_6$ octahedra up to 10 GPa. (c) Atomic coordinates of La as a function of pressure ($y_{La} = 1/4$). The inset shows the evolution of the intensity of the (111) reflection normalized to the (101) peak. (d) Mn-O distances of the distorted MnO$_6$ octahedra as a function of pressure.
pronounced for the Mn-O2 (a) distance which relates to the large a axis compressibility at low pressures. Extrapolation of the data suggests all Mn-O bond lengths become nearly equal around 18 GPa, which coincides with the occurrence of the a axis compression anomaly. This equalization of the Mn-O distances means that the cooperative Jahn-Teller effect is reduced with increasing pressure, a process which appears to be completed near 18 GPa.

Raman spectroscopy (Fig. 3) shows that the structural changes are more complex than indicated by the x-ray data which reflect the average long-range order. The $B_{2g}$ Raman peak (1) at 610 cm$^{-1}$ (in-phase O2 stretching mode [15]) shifts towards higher energy and loses intensity with increasing pressure. From the extrapolation of the intensity-versus-pressure data, it is expected to vanish near 18 GPa. A new peak (2) starts to appear near 7 GPa, approximately 45 cm$^{-1}$ higher in energy than peak (1). The intensity redistribution from the O2 stretching mode (1) to the new higher-energy peak (2) shows that a sluggish transition occurs that is not evident from the x-ray data.

The pressure range 7–18 GPa, in which the Raman intensity redistribution takes place, coincides with that marked by the anomalies of the c and a lattice parameters. Together with the absence of distinct changes of atomic positions around 7 GPa, these findings suggest the following scenario: After compression of the sample up to 7 GPa, domains start to form. In these domains the MnO$_6$ octahedra adopt a less distorted, contracted shape which results in the new higher-energy Raman peak. The lattice parameters of the two phases are very similar since no peak splitting is observed in the diffraction experiment. This is easily understood as the octahedral contraction can be compensated (with regard to the lattice parameters) by a change of the octahedral tilting.

The combined x-ray and Raman data show that the cooperative Jahn-Teller effect in LaMnO$_3$ is reduced by application of hydrostatic pressure. There is a strong indication that the Jahn-Teller distortion is completely suppressed at 18 GPa.

A pressure-induced insulator–metal transition takes place at pressures much higher than required to suppress the Jahn-Teller effect. It occurs at ~32 GPa as evidenced by optical reflectivity and electrical resistance measurements (Fig. 4). The broad spectral feature around 2 eV [Fig. 4(a)] corresponds to an optical transition and a related gap near 1 eV, consistent with the insulating nature of LaMnO$_3$ at ambient pressure. Up to 18 GPa—i.e., in the pressure range where the suppression of the Jahn-Teller distortion occurs—only small changes of the optical response are observed. Above 30 GPa, the near-infrared reflectivity increases strongly [inset of Fig. 4(a)] indicating an insulator-to-metal transition in agreement with the electrical resistance experiments. At 32 GPa these show a change in sign of the resistance derivative, $dR/dT$, namely from semiconductor to metal behavior [Fig. 4(b)]. In addition, a sharp drop of the ambient-temperature resistance occurs at the same pressure [inset of Fig. 4(b)]. The system retains a rather high resistance, i.e., it is a “poor” metal.

Our results suggest the existence of three distinct regimes: (i) an insulating one with JT distortion and orbital ordering [<18 GPa], (ii) an intermediate one with suppressed JT distortion and no orbital ordering, but still insulating [18–32 GPa], and (iii) a metallic phase without JT effect [>32 GPa]. For a certain range of pressures undoped LaMnO$_3$ thus exists in an insulating state which is not caused by the JT effect. This supports the view that LaMnO$_3$ basically is a Mott (or charge-transfer) insulator.

The observed decrease of the Mn-O distances under pressure and the decreasing octahedral tilting both enhance
the Mn-O-Mn interactions and hence the bandwidth arising from the $e_g$ orbitals. In the intermediate insulating state the $e_g$ electrons are already sufficiently delocalized to suppress the JT effect, but still not itinerant enough to make the system metallic. The energetics in such an intermediate regime have been discussed by Goodenough [16]. It cannot be excluded from our data that the stabilization of this insulating state involves other instabilities, e.g., a charge-density wave formation similar to that observed in the isoelectronic ($t_{2g}^3e_{g}^{1}$) Fe$^{4+}$ oxide CaFeO$_3$ [17]. In contrast to the CMR materials, the insulator-metal transition in LaMnO$_3$ is driven by an increased bandwidth and not by chemical doping.

The notion of delocalization of $e_g$ (or $t_{2g}$) electrons without metallization seems also of relevance for other transition metal oxides with Jahn-Teller electron configurations, e.g., Fe$^{3+}$ oxides [18], rare earth nickelates ($t_{2g}^6 e_{g}^{1}$ Ni$^{3+}$ ions) [19], and LaTiO$_3$ ($t_{2g}^1$ Ti$^{3+}$ ions) [20]. At ambient pressure many of these materials are close to the insulator-metal borderline and some reveal insulating states without signs of orbital ordering. However, the noncontinuous variation of the structural and electronic properties across the series of these oxides with varying chemical composition has hindered a clear recognition of their correlations.

The pressure-induced changes described above are expected to alter the magnetic properties of LaMnO$_3$. The suppression of the orbital order may lead to a collapse of the A-type antiferromagnetic order observed at low temperature. The increasing delocalization of the $e_g$ electrons which show Hund’s rule coupling to the more localized $t_{2g}$ electrons, possibly favors magnetic structures with enhanced ferromagnetic interactions (e.g., a spiral or ferromagnetic spin arrangement).

In conclusion, we have studied the structural changes of undoped LaMnO$_3$ under high hydrostatic pressure and their relation to the electronic properties. The pronounced cooperative Jahn-Teller distortion and the GdFeO$_3$-type distortion (octahedral tilting) decrease with increasing pressure. We infer that the JT effect and the concomitant orbital order are completely suppressed at 18 GPa. On the other hand, the system remains insulating to $\sim 32$ GPa where it undergoes a bandwidth-driven insulator-metal transition. The observation of an insulating state with suppressed JT effect supports the view that LaMnO$_3$ is a Mott (or charge-transfer) insulator, the JT distortion rather being a consequence of the localization of the $e_g$ electrons than its origin. Delocalization of electron states which suppresses the JT effect, but is too weak to make the system metallic, appears to be a key feature of insulating transition metal oxides with quenched JT distortion.