Pressure induced magnetic phase separation in La$_{0.75}$Ca$_{0.25}$MnO$_3$ manganite

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Abstract
The pressure dependence of the Curie temperature $T_C(P)$ in La$_{0.75}$Ca$_{0.25}$MnO$_3$ was determined by neutron diffraction up to 8 GPa, and compared with the metallization temperature $T_{IM}(P)$ (Postorino et al 2003 Phys. Rev. Lett. 91 175501). The behavior of the two temperatures appears similar over the whole pressure range, suggesting a key role of magnetic double-exchange also in the pressure regime where the superexchange interaction is dominant. The coexistence of antiferromagnetic and ferromagnetic peaks at high pressure and low temperature indicates a phase separated regime which is well reproduced with a dynamical mean-field calculation for a simplified model. A new $P$–$T$ phase diagram has been proposed on the basis of the whole set of experimental data.

Perovskite-like manganites La$_{1-x}$Ca$_x$MnO$_3$ (LaCa$_x$) exhibit a variety of physical properties depending on the Ca concentration $x$. The strong correlation among the magnetic, electronic, orbital and transport properties of manganites makes these systems particularly sensitive to external perturbations, such as temperature variation, application of magnetic field or high pressure (HP) [1, 2]. The most popular phenomenon is the colossal magneto-resistance (CMR) [3] observed over the 0.2 < $x$ < 0.5 range. Here, the system shows a transition from a high temperature paramagnetic (PM) insulating phase to a low temperature ferromagnetic (FM) metallic one and its properties can be described by two competing mechanisms: the double-exchange (DE) [4] mechanism and the Jahn–Teller (JT) effect [5]. The DE model, which couples magnetic and electronic degrees of freedom, qualitatively explains the observed transition and the contiguity between the insulator to metal transition temperature $T_{IM}$ and the Curie temperature $T_C$. More realistic modeling is only obtained by introducing the JT mechanism with its charge localizing effect [5].

HP techniques have been successfully employed to investigate the role of JT structural distortion on manganite properties. The idea is that lattice compression reduces the JT distortion [6, 7], and increases the hopping integral $t$, thus favoring the onset of the metallic phase [8]. Several manganites show indeed an increase of $T_{IM}$ on applying pressure up to 2–3 GPa [9, 10]. Nevertheless, experiments at higher pressures cast doubts on the above scheme [11, 12].
Several HP experiments have been carried out on LaCa$_x$ manganites. In particular, in LaCa$_{0.25}$ $T_{IM}(P)$ was found to increase linearly only up to $P \approx 3$ GPa, to bend down above 6 GPa and to approach an asymptotic value close to room temperature [8, 13]. An antiferromagnetic (AFM) superexchange (SE) interaction between the Mn magnetic moments [14], which are formed by localized $t_{2g}$ electrons, was proposed to be responsible for the anomalous $T_{IM}(P)$ evolution at HP [15]. This peculiar pressure behavior can be ascribed to a competition between the DE and SE interactions, which is responsible for the AFM order observed away from the CMR concentration region at ambient pressure. Since the strength of the DE is proportional to the hopping integral $t$ and SE is proportional to $t^2$, on increasing pressure (i.e. $P$) the role of SE versus DE is continuously enhanced and it is expected to become the dominant interaction in the HP regime [8, 15]. The pressure dependence of the magnetic transition was recently investigated by neutron diffraction in LaCa$_{0.33}$ [16] and LaCa$_{0.25}$ [17] over the 0–4 GPa range and an almost linear $P$-dependence of $T_C$ was observed. In LaCa$_{0.25}$ rather close values of $T_{IM}$ and $T_C$ [17] were found over the whole range. As a confirmation of the role of SE, evidence of AFM order coexisting within the FM phase was also obtained at low temperature and HP [16, 17].

The suppression of the long range FM order at HP (around 23 GPa) in LaCa$_{0.25}$ was deduced by x-ray magnetic dichroism data [18]. The remarkable compression of MnO$_6$ octahedra along the $b$ axis and the anomalous change in the lattice strain at around 23 GPa together with the monotonic decrease of the FM moment with pressure, suggested indeed a transformation from an orbitally disordered FM phase to an orbitally ordered AFM phase [18]. The coexistence of the two magnetic phases in the pressure range between 2 and 23 GPa was conjectured [18]. It is worth noting that although the tendency toward mixed phases, whether structural or magnetic, was recently observed in several manganites at ambient [19] and high pressures [6, 20–22], the theoretical investigation of this phenomenon was rather limited.

Although LaCa$_{0.25}$ is the most extensively investigated manganite system under pressure, no experimental data are available on $T_C(P)$ over the $P$ range where $T_{IM}$ is no longer linear and the SE mechanism is dominant over the DE. In this paper we extend the neutron diffraction measurements on LaCa$_{0.25}$ up to 8 GPa in order to clarify the roles and the relative strengths of the DE and SE interactions and the coupling between $T_C$ and $T_{IM}$ in the HP regime. The tendency toward phase separation is modeled by using the simple theoretical approach successfully employed in [15].

The neutron diffraction experiment was carried out at the LLB (Saclay, France) using the G6-1 two-axis powder diffractometer with a selected incident neutron wavelength of $\lambda = 4.74$ Å. The diffraction patterns were collected over the 1.5–300 K temperature range along several isobaric paths. Details about the cell are reported in [23]. Sapphire anvils were used at 2.1, 3.9, and 6.0 GPa and, diamond anvils were employed at 8 GPa. The sample volume ranged from several millimeters (sapphire anvils) to 0.01 mm$^3$ (diamond anvils). The sample, prepared by a solid reaction method, was finely milled and a mixture of sample and NaCl salt (1:2 volume proportion) was loaded into the gasket hole together with small ruby spheres for pressure calibration.

Ambient pressure data were collected over a wide $d$-space range, 2.5 $\AA < d < 54$ Å (20 = 5°–140°), using two detector positions. Diffraction patterns at high and low temperature are shown in the inset of figure 1(a). At low temperature, the strong increases of the peak intensities at $d = 38$ Å and $d = 7.38$ Å are ascribed to AFM order. The calculated positions of the Bragg reflections are also shown: the two upper sets correspond to the nuclear and magnetic phase in agreement with [17, 18], the two lower sets are associated with the second structural and magnetic phase. Inset: FWHM of AFM and nuclear peaks versus pressure at $T = 1.5$ K.

**Figure 1.** (a) Diffraction pattern and Rietveld refinement at $P = 0$ and $T = 1.5$ K. Inset: comparison between the $P = 0$ diffraction patterns collected at $T = 240$ and 1.5 K. (b) Diffraction patterns at 6 GPa collected at $T = 280$ and 1.5 K. The peaks at $d = 3.47$ and $d = 7.38$ Å are ascribed to AFM order. The calculated positions of the Bragg reflections are also shown: the two upper sets correspond to the nuclear and magnetic phase in agreement with [17, 18], the two lower sets are associated with the second structural and magnetic phase. Inset: FWHM of AFM and nuclear peaks versus pressure at $T = 1.5$ K.
In order to reduce the acquisition time at HP, we focused on the main peak at $d = 3.87$ Å and diffraction patterns were collected exploiting only one detector position ($2\theta = 12^\circ-91^\circ$ and $3.3 < d < 22$ Å). Data collected at 6 GPa are shown in figure 1(b) where new magnetic reflections are found at $d = 7.38$ Å (0 1 0) and $d = 3.47$ Å (1 1 1). These peaks are unambiguously observed at $P = 3.9$ GPa and upwads, whereas the data collected at $P = 2.1$ GPa do not allow any definitive conclusion. Nevertheless, a new pressure induced peak ($d = 7.47$ Å at 1.5 GPa) was previously reported in reference [17] and ascribed to an AFM order with A-type structure and propagation vector $k = (000)$. This suggests that the AFM peak is probably too weak compared with the signal/noise ratio to be observed in the pattern collected at $P = 2.1$ GPa.

Looking at the present data, a discrepancy is observed between the observed AFM peak position and the expected $d$-spacing calculated on the basis of the lattice parameters. For example, considering the lattice parameters ($a = 5.41$ Å, $b = 7.66$ Å, $c = 5.45$ Å) obtained at 6 GPa, the (0 1 0) AFM peak is expected to be found at 7.66 Å, whereas it is centered at $d = 7.38$ Å (see figure 1(b)). At this point, it is worth noticing that both Kozenklo and Ding observed a uniaxial anisotropic compression of the MnO$_6$ octahedra along the $b$ axis of the orthorhombic structure, which is consistent with this shift of the AFM peak position [17, 18]. These findings suggest that the two magnetic phases, the AFM and the FM, are not associated with the same nuclear phase. Two possible explanations can be proposed: (i) the AFM order is not commensurate with the nuclear phase, as already reported for some manganite compounds [25]; (ii) the AFM order is associated with a nuclear phase with the same $Pnma$ symmetry but different values of lattice parameters.

In support of hypothesis (ii), the positions of nuclear and magnetic reflections were obtained above 4 GPa using Fullprof software (see figure 1(b)) [26]. For example, at 6 GPa two $Pnma$ nuclear structures and two magnetic orders were considered: the first one associated with FM order with the set of lattice parameters reported in references [17, 18] and the second one associated with an AFM order with $a = 5.58$ Å, $b = 7.38$ Å and $c = 5.49$ Å. The AFM unit cell was described by four Mn atoms: $Mn_1 = (00\frac{1}{2})$, $Mn_2 = (\frac{1}{2}00)$, $Mn_3 = (0\frac{1}{2}\frac{1}{2})$, $Mn_4 = (\frac{1}{2}\frac{1}{2}0)$. The magnetic structure is a combination of the $\Gamma_5$ and $\Gamma_7$ representations. The Bragg reflections calculated for the AFM structure (A-type) using the $R_i = (++)$ and $R_i = (+++)$ sequence of magnetic moments and propagation vector $k = (000)$ were well consistent with the experiment as shown in figure 1(b). The magnetic moments lay on the $ab$ plane and they were placed in a way that is similar to that observed in LaMnO$_3$ at high pressure [27]. The fractional volumes of the FM and the AFM phases were obtained for the neutron pattern collected at $T = 5$ K and were found to pass from 87.9% (FM) and 12.1% (AFM) at 4 GPa to 76.3% (FM) and 23% (AFM) at 8 GPa. The FWHMs of the FM (101)/(020) and the AFM peak (010) show opposite behaviors on increasing the pressure: the former increases while the latter decreases (see the inset of figure 1(b)). This behavior is thus consistent with hypothesis (ii), that is lattice compression simultaneously induces both AFM order and a separation between two isostructural nuclear phases.

The emerging scenario is consistent with a well founded physical picture. If the AFM order is driven by the SE interaction, the Mn orbitals are expected to order in a way that reduces the $b$ axis. The connection between the lattice and orbital degrees of freedom, as investigated in several orthorhombic manganites [21, 28, 29], suggests that the development of orbital ordering results in a contraction of the $b$ parameter, and if $b/\sqrt{2} < c < a$ the occurrence of an orbital ordering can be conjectured [28, 29]. On the other hand, if $c > a \simeq b/\sqrt{2}$, orbital disorder is expected. It appears thus reasonable to associate FM and AFM order to orthorhombic phases with large and small $b$ parameters: 7.66 Å and 7.38 Å respectively.

The FM to PM transition can be identified by looking at the temperature dependence of the integrated intensity of the main peak ($d = 3.87$ Å) (inset in figure 2). The results of the refinements do not considerably change on including or excluding the Debye–Waller factor, suggesting that the temperature dependence of the nuclear intensities can be neglected. Therefore, the Debye–Waller factor was neglected over the scattering vector range relevant to the magnetic peaks. After proper background correction, the integrated peak intensities, subtracted by the nuclear contribution, can be reasonably considered proportional to the effective magnetic moments $M$. The temperature dependence of the normalized magnetic moments $M/M_0$ (where $M_0$ is the effective magnetic moment at the lowest $T$) is shown in figure 2 at different pressures.

A rapid increase of $T_C$ on applying pressure is evident over the low pressure range (0–4 GPa), whereas a strongly reduced pressure dependence is observed above 4 GPa. We notice that the observed broadening of the transition can be likely ascribed to strain effects due to pressure gradients. The data were analyzed using a modified Brillouin function to

![Figure 2. Normalized magnetic moments versus temperature (the solid lines are guides to the eye). Inset: temperature dependence of the FM peak $h, k, l = 1, 0, 0$.](image)
describe the temperature dependence of the magnetization, according to the Weiss molecular field theory [30]. To avoid the intrinsic ambiguity of the definition of both $T_C$ and $T_{IM}$, we used the temperature variations $\Delta T$ from ambient pressure $T_C(P=0)$ and $T_{IM}(P=0)$ to compare the pressure dependence of $T_C(P)$ and $T_{IM}(P)$ [8]. As shown in figure 3, the pressure dependence of $\Delta T$ is basically the same for both $T_C$ and $T_{IM}$: a linear increase at low pressure followed by a saturation toward an asymptotic value above 6 GPa. This result further confirms the onset of a pressure-driven localization mechanism that, becoming competitive with the DE delocalizing mechanism at high pressure, strongly affects both the transition temperatures $T_C$ and $T_{IM}$. Moreover, the onset of an AFM state at low temperature coexisting with the FM order confirms the SE-AFM nature of the localizing interaction. This suggests a phase separation scenario at low temperature, as depicted in the inset of figure 3 where a tentative $P-T$ phase diagram is shown. We finally notice that an AFM state at low temperature coexisting with the FM order confirms the SE-AFM nature of the localizing interaction.

In order to understand theoretically whether the pressure induced increase of AFM-SE can, in turn, induce a phase separation, we considered a simplified model for manganites similar to that used in references [15, 31]:

$$ H = -t \sum_{\langle ij \rangle, \sigma} (c_{i, \sigma} \tilde{c}_{j, \sigma} + c_{j, \sigma}^\dagger \tilde{c}_{i, \sigma}) - \mu \sum_{i, \sigma} \tilde{c}_{i, \sigma} \tilde{c}_{i, \sigma} - J_H \sum_{\sigma} \tilde{S}_i \cdot \tilde{S}_j + J_1 \sum_{\langle ij \rangle} \tilde{S}_i \cdot \tilde{S}_j - g \sum_{i} (\tilde{\sigma}_i a_i + a_i^\dagger \tilde{\sigma}_i) + \omega_0 a_i^\dagger a_i. \quad (1) $$

A single band of itinerant electrons with nearest-neighbor hopping $t$ replaces the two $e_g$ bands, and a Holstein coupling to a local Einstein phonon of frequency $\omega_0$ mimics the JT interaction. The DE physics is introduced through an FM coupling between the itinerant band and localized spins $\tilde{S}_i$ associated with the $t_{2g}$ orbitals. The localized spins are, in turn, antiferromagnetically coupled with a coupling constant which is small at ambient pressure and grows with increasing pressure as discussed in reference [15]. We work in the grand canonical ensemble, where the chemical potential $\mu$ determines the particle density in the $e_g$ bands. The density $n = \langle \sum_{i, \sigma} n_i, \sigma \rangle$, where $n_i, \sigma = c_{i, \sigma}^\dagger c_{i, \sigma}$ is related to the Ca doping by the relation $x = 1 - n$.

The study of the thermodynamic instability associated with the phase separation requires us to work in the thermodynamic limit, which can be addressed using the dynamical mean-field theory (DMFT) [32]. We studied the Holstein-DE model (1) at $T=0$ using the DMFT and exact diagonalization to solve the numerical part of the DMFT. We used our implementation of the DMFT, as discussed in reference [33], with exact diagonalization using eight levels in the discretized bath.

Since the aim of this calculation was to understand whether, on general grounds, phase separation can be expected from the competition between AFM and FM, we introduced some safe approximations. In particular we treated the localized $t_{2g}$ spins as classical variables neglecting quantum fluctuations. Moreover, in the light of the experimental suggestions, only the two configurations FM and commensurate AFM ordering were considered, neglecting intermediate orientations and more exotic spin patterns. We computed the total energy for these two phases and for the nonmagnetic phase as a function of the Ca concentration. The effect of pressure was included in the calculations adopting the parameters of reference [15], with the SE coupling scaling as the square of the hopping parameter. Even though our model is too simplified to attempt a quantitative comparison with the experimental phase diagram, it is expected to properly reproduce the competition between magnetic phases which ultimately leads to phase separation.

Phase separation is associated with a negative charge compressibility $\kappa = \partial n/\partial \mu$, which corresponds to a negative curvature of the energy as a function of density (or equivalently of doping). In order to detect phase separation we need to solve the system for various values of Ca concentration and analyze the curvature of the ground state energy around the experimentally relevant case $x = 0.25$. In our case each of the independent solutions (FM, AFM, nonmagnetic) has the correct positive curvature for every value of $x$ (see the curves in the two insets of figure 4).

However, when two curves cross as a function of doping and the system undergoes a first-order transition from one phase to another, the energy has a cusp, and, more importantly, one can lower the energy by dividing the system into a fraction of AFM and a fraction of FM. This is realized through a Maxwell construction (solid black line in the two panels) and physically corresponds precisely to phase separation. In figure 4 we show the pressure versus Ca doping phase diagram obtained with the DMFT.

At zero pressure we find phase separation between AFM and FM only close to $x = 0$ [34]. Our simplified model shows indeed phase separation below $x \simeq 0.16$, while larger...
AFM peaks depicts a phase separation scenario promoted by pressure. This tendency toward a phase separation is properly reproduced, using a simplified theoretical model, indicating that the formation of domains is promoted by pressure.

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Figure 4. $P$–$x$ phase diagram for the Holstein-DE model with parameters from [15]. A pressure dependence line separates a phase separation region from a homogeneous ferromagnetic state. Phase separation is favored by increasing pressure. Insets: the $x$-dependence of the free energy normalized to the bandwidth at $P = 0$ and 6 GPa. The dashed red (blue) line represents the $x$-dependence for the AFM (FM) phase. The solid black line is a Maxwell construction whose boundaries determine the doping range for which phase separation takes place at the chosen pressure.