High-pressure phase diagram in the manganites: a two-site model study

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Abstract. The pressure dependence of the Curie temperature $T_C$ in manganites, recently studied over a wide pressure range, is not qualitatively accounted for by the quenching of Jahn–Teller distortions, and suggests the occurrence of a new pressure-activated localizing process. On the basis of several high-pressure experiments, the antiferromagnetic (AF) interaction between the core spins has been suggested as a good candidate for such a localizing mechanism. We present a theoretical calculation of $T_C$ based on a two-site double-exchange model with electron–phonon coupling interaction and direct superexchange (SE) between the $t_{2g}$ core spins. We calculate the pressure dependence of $T_C$ and compare it with the experimental phase diagram. Our results describe the experimental behaviour quite well only if a pressure-activated enhancement of the AF–SE interaction is assumed.
1. Introduction

Rare-earth manganites (A$_{1-x}$A’$_x$MnO$_3$, where A is a trivalent rare earth and A’ a divalent alkali earth) have been the subject of a renewed interest owing to the discovery of the Colossal magneto-resistance (CMR) [1] exhibited by several of these compounds over the 0.2 ≤ x ≤ 0.5 doping range. The physics underlining the properties of CMR-manganites is very rich and not yet completely understood [2], although CMR is commonly described in the framework of the double-exchange (DE) model [3]. DE qualitatively accounts for the closely related phenomena of CMR and temperature-driven transition from the paramagnetic insulating phase (high temperature) to the ferromagnetic metallic one (low temperature). Nevertheless, the remarkable quantitative disagreement with the experimental data indicates that additional and different physical effects must be introduced [4]. The key role of the Jahn–Teller (JT) effect, i.e. a spontaneous distortion of the MnO$_6$ octahedra, which reduces the energy of the system by lifting the degeneracy of the e$_g$ levels, was pointed out by Millis et al [4] and it is nowadays widely accepted. This effect is naturally associated with a sizeable electron–phonon (el–ph) coupling, which reduces the electron mobility, leading to the formation of small polarons and competing with the delocalizing DE mechanism. The metal–insulator transition temperature $T_{IM}$, which is close and coupled to the Curie temperature $T_C$ via DE, is determined within this framework by the competition between the DE, whose strength depends on the hopping integral $t$, and the el–ph coupling, which is directly linked to the extent of the octahedral JT distortion.

In the last few years, the effects induced by applying very high pressure on manganites have been experimentally investigated. Rather naively, the application of an external pressure is expected to compress the bond length and to symmetrize the MnO$_6$ JT-distorted octahedra with the result of increasing $t$ and reducing the local lattice distortions. Coherently with this idea, it is expected that applied pressure causes an increase in the transition temperature. Early experimental data obtained over a moderate pressure range (0–2 GPa) confirmed the above idea since an almost linear increase in the transition temperature with pressure was observed in a number of manganites [5, 6]. Nevertheless, recent data obtained over more extended pressure ranges have cast doubt on this simple interpretation of the pressure effects [7]–[16]. Several papers report on $T_{IM}(P)$ (and/or $T_C(P)$) showing a three-step behaviour: it is linearly increasing at low pressure, almost constant at intermediate, and rapidly decreasing at high pressure [12]–[16]. The first two steps are also quite evident in La$_{0.75}$Ca$_{0.25}$MnO$_3$, where the $T_{IM}(P)$ curve, recently determined up to 11 GPa [9], shows a linear increase up to $P \approx 3$ GPa and seems to approach an asymptotic value around room temperature beyond $P \approx 6$ GPa. Other experimental findings obtained on the same sample suggest the onset of the high-pressure regime to be accompanied by
dynamical [7] and structural [10] lattice anomalies. Some of the above authors tentatively suggest that the three-step behaviour of the $T_C(P)$ has to be ascribed to the competition between the natural pressure-induced charge delocalization and a new localizing pressure-activated mechanism. The question arising from the present experimental scenario is rather obvious: which mechanism is responsible for the very high-pressure regime behaviour of manganites, i.e. what is contrasting the natural tendency of pressure to increase the charge mobility and $T_C$?

In order to answer the above question, it is worth to notice that a complete description of manganite properties at a microscopic level is further complicated by the presence of an antiferromagnetic (AF)–superexchange (SE) interaction between the $S = 3/2$ spins of the localized $t_{2g}$ electrons, known to be relevant in the electron-doped regime ($x > 0.5$), but which could play a role also in the CMR region [17]. Indeed, starting from theoretical considerations, it has been proposed that the competition between AF–SE and DE could account for some of the magnetic properties of the manganites [18]. Following this approach, a pressure-induced enhancement of the AF interaction could account for the anomalous pressure dependence of the $T_C$. On the other hand, several of the observed features in the very high-pressure regime are, at least, compatible with the above scheme. First of all, quite recently, a direct evidence of an AF order at high pressure in a La-Ca manganite has been obtained by a neutron diffraction experiment [19]. The occurrence of AF interactions in a DE system leads to charge localization, which in turn may favour the coherence of the JT distortions. This picture is consistent with high-pressure x-ray diffraction experiments, in which the onset of a coherent JT distortion has been observed at about 7 GPa in La$_{0.75}$Ca$_{0.25}$MnO$_3$ and other compounds of the La$_{1-x}$Ca$_x$MnO$_3$ series [10, 11]. It is also worth noticing that the onset of the AF phase in LaMnO$_3$ is accompanied by a remarkable softening of the $B_{2g}$-JT phonon [20, 21]. Even in the absence of a real AF ordering, the observed saturation of the same phonon in La$_{0.75}$Ca$_{0.25}$MnO$_3$ at about 7 GPa [7] is consistent with a pressure-induced enhancement of the AF interaction. Finally, the possible role of the AF–SE term in providing an extra localizing channel is quite reasonable, since the SE between $t_{2g}$ orbitals may be thought as proportional to the square of some hopping integral $t_i$ between the $t_{2g}$ orbitals of neighbouring manganese ions. The hopping integral, arising from the overlap of the atomic wavefunctions, is expected to increase with increasing pressure.

In the present paper, we try to establish some theoretical basis to sustain the hypothesis that the pressure-induced localizing mechanism at work in manganites should be ascribed to the reinforced role of the SE interaction in the high-pressure regime. In particular we will focus on the La$_{0.75}$Ca$_{0.25}$MnO$_3$ compound, the only one, at present, for which an extended phase diagram is available [9] together with an almost complete optical [7]–[9] and structural [10] characterization at high pressure. In order to compare the experimental phase diagram with theoretical predictions, we need a model which contains, besides the standard DE and el–ph coupling, also an AF–SE coupling between the $t_{2g}$ core spins.

An extremely simple, yet efficient, model to compute $T_C(P)$ is the two Mn-site cluster, which represents the minimal model including DE, el–ph coupling, and SE interactions. The simplicity of this model enables us to carry out exact calculations at finite temperature, which are fundamental to describe the experimental $P$–$T$ phase diagram.

The two-site model (TSM) presented here has already been applied in [22], where it has been shown to successfully catch the relevant physics of manganites at $T = 0$. Despite the extremely small size of the cluster, this system is indeed sufficient to describe the competition between delocalized and localized states, as well as the possibility of ferromagnetic and AF alignment of neighbouring core spins. Here we extend the study to finite temperature and discuss the
dependence on pressure of the various parameters in the Hamiltonian. In this way we treat, at the same level, the quenching of the JT interactions and the role of AF–SE coupling in determining the pressure dependence of the metal–insulator transition. We show that the experimental results are well described if the AF–SE interaction is assumed to increase with pressure.

2. Model and calculations

The TSM has been extensively employed in the study of polaronic systems, since it is the simplest model able to describe the crossover from a metal to an almost localized small polaron, which is reflected in both the ground state \[23, 24]\ and the spectral properties \[25, 26]\ . The DE-TSM including el–ph coupling has been already studied at \(T = 0\) \[22]\ and its relevance to the case of CMR manganites has been discussed \[22, 27, 28]\ . In particular, the correct ground state has been obtained in several coupling regimes. The qualitative difference between quantum \((S = 3/2)\) and classical \((S = \infty)\) spin cases was also pointed out, showing the importance of quantum fluctuations of the core spins in a proper study of manganites \[22]\ . In the present paper, we extend the model of \[22]\ to finite temperature and focus our attention on the temperature-driven crossover from paramagnetic to ferromagnetic ordering occurring in manganites. In such a minimal cluster, no phase transition with long-range order can occur but, as shown in the following sections, the model allows us to infer predictions on possible instabilities in the thermodynamic limit.

The Hamiltonian of our TSM reads:

\[
H = -t \sum_\sigma (c_{1,\sigma}^\dagger c_{2,\sigma} + c_{2,\sigma}^\dagger c_{1,\sigma}) - J_H \sum_{i=1,2} \vec{\sigma}_i \cdot \vec{S}_i + J_1 \vec{S}_1 \cdot \vec{S}_2 - g (n_1 - n_2) (a + a^\dagger) + \omega_0 a^\dagger a.
\]

(1)

In the electronic part (first three terms), \(t\) is the hopping integral between the \(e_g\) levels, \(c_{i,\sigma}^\dagger (c_{i,\sigma})\) is the creation (annihilation) operator for an electron of spin \(\sigma\) on site \(i\), \(J_H\) is the Hund’s rule coupling, \(\vec{\sigma}_i = c_{i,\alpha}^\dagger c_{i,\beta}^\dagger c_{i,\beta} c_{i,\alpha}\) is the spin operator on site \(i\) (\(\vec{\sigma}_{\alpha\beta}\) are the Pauli matrices), \(\vec{S}_i\) is the local spin \((|\vec{S}_i| = 3/2)\) due to localized \(t_{2g}\) core electrons on site \(i\), and \(J_1\) is the AF–SE coupling. The phonon contribution (last two terms) contains an Holstein coupling and an harmonic term, where \(g\) is the electron–phonon coupling, \(n_i = \sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma}\) is the electron number operator at site \(i\), and \(a^\dagger (a)\) creates (annihilates) an Einstein phonon of frequency \(\omega_0\), coupled to the density difference between the two sites. The above form of the el–ph coupling is equivalent to local phonons coupled to the on-site electron density \(n_i\), after eliminating the symmetric phonon mode which couples to the total density \[22]\ . For the sake of simplicity, we replace the JT coupling with the standard Holstein el–ph coupling. It has been shown that, as far as the evaluation of \(T_C\) is concerned, the Holstein coupling in a single orbital model gives results extremely close to a two-orbital model with JT interactions \[29]\ . The independent parameters of this model are \(J_H/t, J_1/t, \omega_0/t\), and the dimensionless el–ph coupling \(\lambda = 2g^2/\omega_0 t\). As already mentioned, the extreme simplicity of the model does not require further approximations and allows for an exact solution for arbitrary values of the parameters. As an example, the quantum nature of phonons and core spin can be fully taken into account.

In the present calculation we will consider the case of a single electron on the two sites, which corresponds to a filling \(x = 0.5\). This point must be always kept in mind in the comparison with the experiments, which have been performed for \(x = 0.25\), a filling obviously unavailable.
on the two-site cluster. In the situation we study, the Hamiltonian (1) has a very small \((64 \times 64)\)
electronic Hilbert space (including the quantum \(S = 3/2\) spins of the \(t_{2g}\) electrons), while the infinite phonon Hilbert space necessarily requires a truncation up to some maximum phonon number \(n_{\text{ph}}\). Except from the extreme adiabatic case \((\omega_0/t \ll 1)\) and/or extreme multiphononic regime \((\lambda t/\omega_0 \gg 1)\), where a really large number of phonons can be excited, convergence of the relevant states can be, in general, achieved for a relatively small \((<100)\) \(n_{\text{ph}}\). In the non-adiabatic and intermediate coupling regime, a complete diagonalization of (1) can be carried out numerically. In the case of manganites, where we can estimate \(\omega_0/t \approx 0.5\) and \(\lambda \approx 1\) (see below), the convergence for the low-energy states is achieved already at \(n_{\text{ph}} = 10\).

The complete diagonalization of \(H\), i.e. the determination of all eigenvalues \(E_n\) and eigenvectors \(|\psi_n\rangle\), enables the calculation of the thermal average of the nearest-neighbour spin correlation operator \(\mu = \langle \vec{S}_1 \cdot \vec{S}_2 \rangle / S^2\) as:

\[
\mu(T) = \frac{\sum_n \langle \psi_n | \mu | \psi_n \rangle \exp \left(-E_n/T\right)}{\sum_n \exp \left(-E_n/T\right)}.
\]

This quantity measures the short-range magnetic correlations and it is positive for ferromagnetic phases, negative for AF, and vanishes in the high-temperature paramagnetic phase. As we will show in the next section, a simple analysis of the temperature dependence of the spin correlation \(\mu(T)\), allows us to give a reliable estimate of \(T_C\). The choice of this ‘short-range’ estimator of \(T_C\) is, in our opinion, preferable to thermodynamic estimates in our TSM. The reliability of the TSM in the case of manganites can also be assessed through the analogy with a completely different theoretical approach, the dynamical mean field theory (DMFT) [30], which has been applied to a lattice model for the manganites by Millis et al [31]. The DMFT is a powerful non-perturbative approach which freezes spatial fluctuations, but fully retains the local (single-site) quantum dynamics, and becomes exact in the limit of infinite coordination [30]. The DMFT maps the original lattice model in the thermodynamic limit onto a self-consistent impurity model which interacts with a quantum bath. As already discussed in [22], we emphasize the conceptual analogy of these two approaches. In the TSM, the quantum nature of the problem is also completely retained, and each of the two sites ‘feels’ the presence of the other site similarly to the way the impurity site feels the bath within DMFT. We stress that, within the DMFT approach, the system is in the thermodynamic limit. Both the methods, despite their differences, are thus expected to well describe the physics of short-range correlations in manganites. The choice of the TSM allows us to easily include the nearest-neighbour SE–AF interaction, which is instead inaccessible by the single-site DMFT and requires an extended-DMFT study, where the dynamical spin correlation function is also self-consistently evaluated [30], or a cluster-DMFT approach, which retains short-range dynamical correlations, but substantially increases the computational effort [32].

3. Pressure dependence of \(T_C\)

In order to carry out the comparison between the experimental results reported in [9] and the \(T_C(P)\) values which can be determined using the TSM, we need to know the pressure dependence of the input model parameters \(t(P)\), \(J_H(P)\), \(\omega_0(P)\), \(\lambda(P)\) and \(J_1(P)\) for \(\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3\) at least over the 0–11 GPa pressure range. In [33] the hopping integral \(t\) and the Hund’s coupling
Figure 1. Pressure dependence of the hopping integral (dashed line) and of the adimensional electron–phonon coupling (solid line, see text).

\( J_H \) for \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) \((x = 0.33)\) have been derived from first principle calculations as a function of \( a/a_0 \), where \( a \) is the cubic lattice parameter and \( a_0 \) its ambient pressure value. It is reasonable to assume the same dependence of \( t \) upon \( a \) in the \( x = 0.33 \) and \( x = 0.25 \) materials up to an overall factor, namely \( t_{x=0.25}(a/a_0) = C_{t_{x=0.33}}(a/a_0) \). The proportionality factor \( C \) can be evaluated exploiting the proportionality between \( t \) and \( T_C \) at \( P = 0 \) [2], i.e., through the relation \( t_{x=0.25}/t_{x=0.33} = T_C(x = 0.25)/T_C(x = 0.33) \). The pressure dependence of the Hund’s coupling \( J_H \) can be safely assumed to be identical for \( x = 0.25 \) and \( x = 0.33 \) compounds, since \( J_H \) is much larger than the other energy scales, and the results of the calculation are therefore only very weakly dependent on its variations, as we explicitly tested. Finally, using the lattice parameter \( a(P) \) recently measured over the 0–15 GPa pressure range for \( \text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3 \) [10], the \( a/a_0 \) dependence can be simply converted into a pressure dependence. The increase of the hopping integral \( t(P) \) as a function of pressure is plotted in figure 1 in the relevant pressure range (about 12% at 12 GPa). For consistency, we also used the zero-pressure values from [33], even if many alternative estimates of those quantities are available. Namely, we assume \( t(0) \approx 0.20 \text{ eV} \). \( J_H(0)/t(0) = 12.8 \). We emphasize that there is no agreement in the literature on the estimates of \( J_H \), with results ranging from 1 to 3 eV [34]–[37]. Despite our estimate lies on the high part of this range, we used the value given in [33] in order to be consistent with the pressure dependence computed in the same paper. We explicitly checked that the results depend weakly on this ratio as long as \( J_H \) is the largest scale.

The pressure dependence of the JT phonon frequency \( \omega_0(P) \), directly obtained from Raman measurements carried out over the 0–14 GPa range [7], is also useful to get an estimate for \( \lambda(P) \). For a JT mode, it is reasonable to assume that the el–ph coupling \( g \) is given by

\[
g = \sqrt{2M\omega_0} \frac{dt(a)}{da},
\]

where \( M \) is the ionic mass. Using the above set of pressure-dependent parameters, the estimate for the pressure dependence of the adimensional el–ph coupling \( \lambda = 2g^2/\omega_0t \) can be obtained. The resulting \( \lambda(P) \) is plotted in figure 1. The zero-pressure value thus obtained, \( \lambda(0) = 1.04 \), can be checked against an independent estimate of \( g \). The typical JT distortion \( x_0 = \langle x \rangle = 1/\sqrt{2M\omega_0}\langle(a + a^\dagger)\rangle \) can be estimated, in the polaronic regime, as \( x_0 = \sqrt{2/M\omega_0g/\omega_0} \). Using the value \( x_0 = 0.09 \AA \) for \( \text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3 \) at \( P = 0 \) [38], one has
\[ \lambda(0) = 0.94, \] which compares well with the previous estimate. The remarkable pressure-induced reduction of \( \lambda(P) \) (about 50\% at 12 GPa) is consistent with the observed enhancement of the metallic character of the system and with the increase of the transition temperature \( T_C \) [7, 9].

The last ingredient is the AF–SE coupling \( J_1 \) with its pressure dependence. To our knowledge, no direct estimate of this parameter, either experimental or theoretical, is available. An estimate of the zero-pressure value of \( J_1(P) \) can be obtained by simply imposing the calculated \( T_C(0) \) equal to the known experimental value of 220 K for \( \text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3 \) at zero pressure [2]. It is worth to notice that the value of \( J_1 \) so obtained is of the same order of magnitude as that estimated by the Néel temperature in the \( x = 1 \) [39]. Unfortunately, we were not able to find any estimate of the pressure dependence of \( J_1 \) in the literature as well as of the Néel temperature or other related quantities. This leads us to consider and compare a few options for this pressure dependence, as we detail below.

In figure 2, we show \( \mu(T) \) (see (2)) calculated in the TSM using the above-described estimates for the various parameters. The crossover from a ferromagnetic state at low temperature, with a large positive value of \( \mu \), to a paramagnetic state at high temperature with \( \mu \to 0 \) is evident. The absence of an abrupt variation of \( \mu(T) \) is expected since the real-phase transition occurring in the thermodynamic limit cannot take place in a finite system and it is replaced by a smooth crossover. In the TSM the crossover is quite broad and the estimate of the critical temperature is not completely straightforward and implies some degree of arbitrariness. For this reason, we propose, and compare, two different methods for evaluating \( T_C \). The first one, the half-maximum method, simply defines \( T_C \) as the temperature for which \( \mu(T_C) = [\mu(0) - \mu(\infty)]/2 = \mu(0)/2 \), i.e. for which the spin correlation becomes one-half of its zero-temperature value. The second method is based on a linear extrapolation around the inflection point of the \( \mu(T) \) curve.

**Figure 2.** Temperature dependence of the nearest-neighbour spin correlation (thick solid line, see text), calculated for \( \lambda = 1.04, \; j_H/t = 12.8, \; \omega_0/t = 0.39 \) and \( J_1/t = 0.047 \). Thin solid and dashed lines represent the half-maximum and linear extrapolation methods for determining \( T_C \), respectively (see text).
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These two methods are schematically represented in figure 2 from which it is apparent that the latter method provides a higher value for $T_C$. Interestingly, the two estimates of $T_C$ are actually proportional over a wide range of parameter values. Therefore, the choice of one method basically affects only the absolute value of $T_C$ and not the internal comparison between results obtained with a given estimator. In the following, we use the half-maximum estimate to determine the effect of pressure on $T_C$. It is important to note that the precise $J_1(0)$ value is influenced by the method chosen for determining $T_C$. For example, the determination of $T_C$ with the half-maximum method leads to $J_1(0) = 0.047t(0)$, whereas the linear extrapolation provides $J_1(0) = 0.060t(0)$. The slight difference between the zero-pressure values is not important since we are mostly interested in the pressure dependence of the parameters rather than in their absolute values.

As mentioned before, since the pressure dependence of $J_1$ is unknown, we have carried out calculations of $T_C(P)$ for three different pressure dependencies of $J_1(P)$, namely: (i) $J_1(P) = $ const.; (ii) $J_1(P) \propto t(P)$ and (iii) $J_1(P) \propto t^2(P)$. These choices are quite arbitrary, but bearing in mind that $t(P)$ is an increasing function of the pressure (see figure 1), the three choices correspond to reduce, keep constant and increase the ratio $J_1/t$ upon increasing pressure. Therefore the study of cases (i)–(iii) allows us to compare the effect induced on $T_C$ by an AF interaction with either strong or weak pressure dependence. A more quantitative analysis would require an independent model of the pressure dependence of $J_1$ based, e.g., on ab initio studies, but this lies beyond the purpose of the present paper.

The results of the TSM calculations together with the experimental data from [9] are shown in figure 3. Before discussing the present results against the experimental one, we would like to point out the validity of the TSM approach by comparing its results with those provided by the DMFT in which only a DE term (classical core spins) and a JT-like el–ph interaction (classical...
phonons) have been used [31]. Using the present estimates for $\lambda(P)$ and $t(P)$, $T_C(P)$ can be readily obtained from the results of the DMFT calculations reported in [31]. In figure 3 these $T_C(P)$ values, divided by a factor 1.1 to agree to the $T_C(0)$ experimental determination, are also shown. The use of such a small factor gives us confidence about the reliability of the present model parameter estimates at ambient pressure. The comparison between the pressure dependence of the theoretical results shows that DMFT and TSM case (ii) provide extremely close results (see figure 3). To comprehend the reasons for such a remarkable agreement, it is worth to bear in mind that the pressure dependence in the DMFT approach is basically determined by $\lambda$, while in our TSM $\lambda$, $\omega_0$ and $J_1$ depend on $P$. Since $\omega_0/t$ is only weakly dependent on pressure, the choice $J_1 \propto t$ leads to a TSM in which the pressure dependence is substantially determined by $\lambda$ only, as in the DMFT estimate. This argument explains the observed equivalence between the two approaches and, above all, it points out how the pressure dependence of the el–ph interaction alone does not provide a satisfactory description of the observed experimental high-pressure behaviour (see figure 3).

The pressure dependence of the AF interaction remarkably affects the calculated $P–T$ phase diagram. At low pressures the results from (i) and (ii) nicely follow the experimental $T_C(P)$, whereas the case (iii) gives critical temperatures systematically lower than those of experimental. On increasing the pressure, $T_C(P)$ increases too rapidly in the first two cases while in the third case it closely follows the experimental data up to 11 GPa. It is therefore crucial to have an enhanced (though still small) AF effect to explain the experimental observations.

We could try to justify the proportionality between $J_1$ and $t^2$ by proposing that $J_1$ is built by virtual processes associated involving both $J_H$ and the Hubbard repulsion, but we prefer to simply propose the $t^2$ dependence as the simplest (sensible) one that provides an increase of $J_1$ under pressure. More realistic descriptions of the pressure dependence of $J_1$ require further studies. In summary our results clearly show that the effects of pressure are not only limited to a reduction of the el–ph coupling but that a remarkable pressure dependence of the AF interaction is necessary to account for the experimental behaviour.

The present model can be conversely exploited to extract an ‘experimental’ pressure dependence of the AF term using the experimental $T_C(P)$ values. This simply amounts to determine, at each pressure, the value of $J_1(P)$ which provides the correct experimental $T_C(P)$. In Figure 4, the $J_1(P)/J_1(0)$ values so obtained are shown in comparison with the $t(P)/t(0)$ and $t^2(P)/t^2(0)$ values. Although a sort of crossover from the $t$ to the $t^2$ behaviour can be observed as the pressure is increased, it is apparent that the latter quantity shows an overall better agreement than the investigated pressure range. The above results strengthen, from a theoretical point of view, the hypothesis that the saturation of $T_C(P)$ observed above 6–7 GPa [9] can be ascribed to the onset of a regime in which the AF interaction is no more negligible and competes with the DE.

The $J_1(P) \propto t^2(P)$ dependence suggests that, upon increasing the pressure, the system evolves from a regime dominated by DE, where the bond compression leads to an increase of $T_C$, to an intermediate regime, where $T_C$ is almost constant and independent of pressure, owing to the competition between SE and DE, and eventually to a very high-pressure regime dominated by the SE contribution where $T_C$ starts decreasing. This picture is absolutely consistent with the pressure dependence of $T_C(P)$, recently observed in several manganites where the three regimes are apparent [12]–[16]. We want to point out that in the above cases the onset of the saturation regime, where $T_C$ is almost pressure independent, takes place at a pressure significantly lower than that observed in the presently investigated La$_{0.75}$Ca$_{0.25}$MnO$_3$ [9]. This difference can be ascribed...
to the presence of a strong coupling and/or high-cation disorder which have been shown to have strong effects on the pressure dependence of $T_C$ [9].

4. Conclusions

We studied the evolution of the transition temperature of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ with pressure by exactly solving a two Mn-site model which contains all the relevant microscopic interactions at work in manganites. The theoretical results have been compared with the phase diagram recently measured over the 0–11 GPa pressure range [9]. As input parameters for the model, we used pressure-dependent data available in the literature, except for the direct AF–SE between the $t_{2g}$ spins, for which, in absence of experimental estimates, we compared three different pressure dependencies. We have shown that the pressure-dependence law for $J_1$ is indeed crucial to obtain a good agreement with the experiment. Neglecting the effect of pressure on the AF–SE term leads in fact to a sizeable overestimate of the Curie temperature for $P > 6$ GPa. On the other hand, the theoretical results follow rather closely the experimental data over the whole pressure range for $J_1(P) \propto t^2(P)$, while the calculation largely overestimates the critical temperature at large pressures if a weaker pressure dependence of $J_1$ is assumed.

Recent high-pressure neutron diffraction data [19] clearly indicate the appearance of AF ordering in a ferromagnetic manganite on increasing pressure. The idea of a pressure-activated AF interaction is also compatible with other experimental evidence of the onset of co-operative JT effect [10, 11] and phonon softening [7] in the very high-pressure regime. These findings suggest that the observed $T_c(P)$ saturation at high pressure could be ascribed to the AF–SE coupling. Our results support this hypothesis giving a theoretical evidence of how an AF coupling with a $t^2$ dependence can account for the observed experimental behaviour.

Figure 4. Pressure dependence of $J_1$ obtained from a best fit of the experimental data with the TSM (open circle) compared with the $J_1 \propto t^2$ (dashed line) and $J_1 \propto t$ (dotted line) dependences. All curves are normalized to their zero-pressure value. The solid line is a guide to the eye.
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New Journal of Physics 8 (2006) 3 (http://www.njp.org/)
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