Theory of the unusual doping and temperature dependence of photoemission spectra in manganites

Prabuddha Sanyal\textsuperscript{1,2(a)}, Subhra Sen Gupta\textsuperscript{1,3,4}, Nandan Pakhira\textsuperscript{1,5}, H. R. Krishnamurthy\textsuperscript{1,5}, D. D. Sarma\textsuperscript{1,4,5,6} and T. V. Ramakrishnan\textsuperscript{1,7}

\textsuperscript{1} Centre for Condensed Matter Theory (CCMT), Department of Physics, Indian Institute of Science Bangalore 560012, India
\textsuperscript{2} Harishchandra Research Institute - Allahabad 211019, India
\textsuperscript{3} Department of Physics and Astronomy, University of British Columbia - 6224, Agricultural Road, Vancouver, BC V6T 1Z1, Canada
\textsuperscript{4} Solid State and Structural Chemistry Unit, Indian Institute of Science - Bangalore 560012, India
\textsuperscript{5} Jawaharlal Nehru Centre for Advanced Scientific Research - Bangalore 560084, India
\textsuperscript{6} Center for Advanced Materials, Indian Association for Cultivation of Science - Kolkata 700032, India
\textsuperscript{7} Department of Physics, Banaras Hindu University - Varanasi 221005, India

received 28 February 2008; accepted 6 April 2008
published online 15 May 2008

PACS 75.47.Lx – Manganites
PACS 79.60.-i – Photoemission and photoelectron spectra
PACS 71.10.-w – Theories and models of many-electron systems

Abstract – A recent, major, puzzle in the core-level photoemission spectra of doped manganites is the observation of a 1–2 eV wide shoulder with intensity varying with temperature $T$ as the square of the magnetization over a $T$ scale of order 200 K, an order of magnitude less than electronic energies. This is addressed and resolved here, by extending a recently proposed two-fluid polaron–mobile electron model for these systems to include core-hole effects. The position of the shoulder is found to be determined by Coulomb and Jahn-Teller energies, while its spectral weight is determined by the mobile electron energetics which is strongly $T$ and doping dependent, due to annealed disorder scattering from the polarons and the $t_{2g}$ core spins. Our theory accounts quantitatively for the observed $T$ dependence of the difference spectra, and furthermore, explains the observed correspondence between spectral changes due to increasing doping and decreasing $T$.

Copyright © EPLA, 2008

Introduction. – Doped rare-earth manganites, $R_{1-x}A_x$MnO$_3$ ($R$ = rare-earth ion; $A$ = alkaline-earth ion), show exotic properties such as colossal magnetoresistance (CMR)\cite{1} close to a temperature ($T$)-driven ferro-metal (FM) to para-insulator (PI) or para-metal (PM) transition, an extraordinarily rich phase diagram with varying $x$, $T$ and magnetic field ($H$), etc.\cite{2}. Particularly intriguing among their properties is the redistribution of spectral weight over an energy window of several eV in valence band\cite{3,4} and Mn 2$p$ core level\cite{5,6} photoemission spectra (CL-PES), as a function of $x$ and of $T$. The changes in the spectral features with doping, incompatible with even an approximately rigid-band description, suggests qualitative and drastic modifications of the underlying electronic structure with small changes in $x$. Similarly, changes in $T$ affect the spectra over energy ranges 100 times the thermal energy scale and cannot be understood in usual terms. Curiously, changes in spectra with increasing $x$ or with decreasing $T$ show striking similarities\cite{4,5}, suggesting a common mechanism. The effects have been attributed\cite{3,4} to the unusually strong electron-spin and electron-lattice couplings in these compounds, but no specific theory has been proposed till now.

Conventional core-level photoemission calculations, in terms of cluster models\cite{7} or impurity models\cite{8}, can not account for a drastic renormalization of the underlying electronic structure with changing $x$ or $T$. The only known mechanisms\cite{9} that yield $T$ dependent changes in PES are Fermi-edge decoherence (FED) effects due to thermal excitations and Debye-Waller type effects due to the scattering of electrons by phonons. They lead to changes only on energy scales of order $T$ and the Debye temperature, respectively ($\sim$ 10–100 meV), and not over several eV as

\textsuperscript{(a)}E-mail: prabs@mri.ernet.in
observed. Cluster calculations [5] with adjustable coupling parameters, using an MnO₆ octahedron coupled to a single level at the Fermi energy, are able to reproduce the multiplet features of the observed spectra; but no x or T dependence, of the magnitude seen in the experiments, can arise unless the coupling parameters are artificially allowed to vary with x and T.

In this paper we adopt a different approach which is complementary to the above schemes, in that we focus on the x and T dependence, while neglecting details of multiplet structure. We extend the recently proposed two-fluid “ℓ-b” model [10] in a dynamical mean-field theory (DMFT) [11] framework, which has successfully explained several hitherto poorly understood low-energy properties of doped manganites, to include core hole effects. We show that a highly plausible explanation of the anomalous dependence of the core-level PES spectra of manganites emerges as a consequence.

Model. – The active degrees of freedom in the manganites are the twofold degenerate e_g levels, the t_2g core-spins (S_i) of Mn, and the Jahn-Teller (JT) optical phonon modes of the MnO₆ octahedra. There are three strong on-site interactions, viz. the JT electron-phonon coupling which splits the two e_g levels by an energy 2E_JT (∼0.5–1 eV), the ferromagnetic Hund’s coupling J_H between the t_2g and e_g spins (∼2 eV) and the e_g electron Coulomb repulsion U_dd (∼5–7.5 eV) [12]; all larger than the e_g inter-site hopping (t ∼0.2–0.4 eV) [13]. The “ℓ-b” model [10] is an effective low-energy Hamiltonian which implicitly captures the crucial effects of these interactions and the quantum dynamics of the JT phonons. Because of the inhibition of kinetic energy, it is argued that the major fraction [≤ (1 − x)] of the e_g electrons in manganites are polaronically trapped and site localized in states labeled ℓ, with site energy −E_JT, and an exponentially reduced hopping (∼1 meV) which is neglected. However, a small number (∼x per site) of electrons are assumed to be able to access states that remain band-like and mobile (b), because they primarily move around on the remaining fraction ∼ x of undistorted sites (site energy 0) with undiminished hopping t, and are repelled from the polaronic sites because of the large U_dd. The model Hamiltonian is hence written as

\[ H_\text{bath} = -E_{\text{JT}} - \mu \sum_{i,\sigma} n_{i\sigma} - \mu \sum_{i,\sigma} n_{b\sigma} \]

\[ + U_{dd} \sum_{i,\sigma} n_{i\sigma} n_{b\sigma} - t \sum_{\langle ij \rangle,\sigma} (b_i^\dagger b_j + \text{H.C.}) \]

\[ - J_H \sum_i (\vec{S}_i \cdot \vec{S}_i - J_F \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j) \]  

\[ J_F \text{ is a novel ferromagnetic virtual double-exchange (VDE) coupling (∼2 meV) between the core spins, which arises naturally in this picture [10]. The chemical potential, } \mu, \text{ imposes the doping determined filling constraint: } \sum_{\sigma}(n_{e\sigma} + n_{b\sigma}) = (1 - x), \text{ while the relative number of } \ell \text{ and } b \text{ electrons changes with } x \text{ and } T \text{ so as to minimize the free energy.} \]

Method of calculation. – The “ℓ-b” model, with the t_2g core spins (S_i) being approximated as classical vectors (\vec{S}_i), describes mobile b electrons moving in an annealed disordered medium of randomly distributed polaronic sites and core spin vectors. It is similar to the Falicov-Kimball model [14], and is exactly soluble in the DMFT [11] framework, with J_F being treated in the Curie-Weiss mean-field approximation [10,15]. The resulting self-consistent “impurity” model [11] for a specific site, at any temperature T and in the limit of J_H → ∞, depends parametrically on Ω_z (the z-component of the unit vector representing the core-spin) at that site, and can be written as [15]

\[ H_{\text{imp}}(\Omega_z) = - (E_{\text{JT}} + \mu) n_\ell + \vec{J}_F \langle m \rangle \Omega_z + (U_{dd} n_\ell - \mu) \vec{b} \cdot \vec{b} \]

\[ + \int_{-\Delta}^{\Delta} d\epsilon (-\mu) a(\epsilon)^\dagger a(\epsilon) + \int_{-\Delta}^{\Delta} d\epsilon V(\epsilon, \Omega_z) (a(\epsilon)^\dagger \vec{b} + \vec{b}^\dagger a(\epsilon)). \]  

(2)

Here, \[ \vec{J}_F = 2z J_F S^2 \] (z = coordination number) and \[ \langle m \rangle \] is the magnetization. The \[ \{ a(\epsilon) \} \] create a continuum of bath electron degrees of freedom which represent (as an approximate effective medium) the mobile electronic states at the other sites of the lattice [11]. The bath electrons hybridize with \vec{b}, the spinless effective b electron at the chosen site (obtained by a spin projection parallel to the direction of the core spin because of the J_H → ∞ limit). The effective bandwidth 2D of the bath electrons, and the hybridization amplitude \[ V(\epsilon, \Omega_z) \], related to the “bath Green’s function” \[ \hat{G}(\omega, \Omega_z) \] via

\[ G^{-1}(\omega^+, \Omega_z) = \omega^+ + \mu - \int_{-\Delta}^{\Delta} d\epsilon \frac{|V(\epsilon, \Omega_z)|^2}{\omega^+ + \mu - \epsilon}, \]  

(3)

are determined self-consistently in the DMFT [10,11,15] and therefore become x and T dependent.\(^1\)

In order to calculate the Mn 2p core-level PES, we add to this a single “core-hole” level (labeled “c”) of positive energy \( \epsilon_c \approx 647.6 \text{ eV} \) at the “impurity” site [16]. The core hole has an attractive Coulomb interaction \( U_{pd} \) (= -6.5 eV) with both the “\ell” and the “b” electrons. For the purposes of this paper, we approximate the “bath” degrees of freedom as having a discrete grid of N energy levels \( \{ \epsilon_n \} \). We have carried out calculations using both

\[^1\text{As discussed in detail in [10], the hopping of the “b” electrons is increasingly inhibited as } x \text{ decreases or as } T \text{ increases. The first due to the increasing number of random repulsive sites occupied by the “c” polarons, and the second due to the thermal disordering of the } t_{2g} \text{ core spins (to which the “\ell” and “b” spins are enslaved by the large } J_H). \text{ The DMFT treats this effect in a “coherent potential” or “effective medium” approximation. Consequently, the effective bandwidth } 2D \text{ is much smaller than the bare bandwidth } 2D_0 \text{ for small } x \text{ or large } T, \text{ but increases substantially as } x \text{ increases or as } T \text{ decreases.} \]
linear and logarithmic discretization [17]², although only the results of the linear case will be discussed in detail in this paper. The corresponding discrete set of hybridization parameters \( V_r(\Omega_z) \) are given by \( w_r V(\epsilon_r, \Omega_z) \) where \( w_r \) are weights that depend on the grid used [17]. The resulting discretized Hamiltonian reads

\[
H_{CL}(\Omega_z) = -(E_{JT} + \mu)n_t + \tilde{J}_F \langle m|\Omega_z + (U_{dd} \eta - \mu)\hat{b}^\dagger \hat{b} \\
+ \sum_r (\epsilon_r - \mu) a_r^\dagger a_r + \sum_r V_r(\Omega_z) (a_r^\dagger \hat{b} + \hat{b}^\dagger a_r) \\
+ (\epsilon_r - \mu) n_c + U_{pa} n_c \hat{b}^\dagger \hat{b} + n_t).
\]

Both \( n_c \) and \( n_t \) commute with, and hence are conserved in, \( H_{CL} \) (eq. (4)). Hence, its many-particle eigenstates can be obtained separately in each of the 4 possible \((n_c, n_t)\) sectors, \((0, 0)\), \((0, 1)\), \((1, 0)\) and \((1, 1)\), which we label as \((I0)\), \((I1)\), \((F0)\) and \((F1)\), respectively. One can therefore calculate a separate core-hole spectral function \( A_{cc}(\omega; n_t, \Omega_z) \) in each \( n_t \) sector, and for each \( \Omega_z \), as

\[
\sum_{m_f, m_r} \frac{e^{-\beta E_{m_f}}}{Z_{\{m_l\}}} \left( \langle m_l | m_f \rangle \right)^2 \times \delta (E_{m_f} - E_{m_l} - \hbar \omega) \]

Here \( m_f, m_r \) label the many-particle eigenstates of \( H_{CL} \) in the \( n_c = 0 \) and \( n_t = 1 \) sectors, respectively, for the specified \((n_c, \Omega_z)\). The full core-hole spectrum is given by the (annealed) weighted average

\[
A_{cc}(\omega) = \sum_{n_t} \int_{-1}^{1} d\Omega_z W_{n_t}(\Omega_z) A_{cc}(\omega; n_t, \Omega_z).
\]

Here \( W_0(\Omega_z) \) and \( W_1(\Omega_z) \) are statistical weights obtained as \( W_{n_t}(\Omega_z) = Z(n_1, n_c = 0, \Omega_z) / Z \) in terms of \( Z(n_c, n_t, \Omega_z) \), the constrained partition functions, calculated for \( n_c = 0 \) and for particular values of \( n_t \) and \( \Omega_z \); and \( Z \) is the total partition function.

The Boltzmann factors in the above expression for \( A_{cc}(\omega) \) give rise to the afore-mentioned FED effects in PES, which are very weak. However, special to our model, and hence to manganites, are two other, unconventional, sources of \( T \) and \( x \) dependence which are much larger: first, the statistical weights \( W_0 \) and \( W_1 \) are dependent on \( x \) and \( T \); second, and more important, as we show below, the spectra for each \((n_t, \Omega_z)\) themselves change with \( x \) and \( T \), with redistribution of spectral weights over scales of eV, because the self-consistent hybridization parameters \( V_r(\Omega_z) \) are strongly \( x \) and \( T \) dependent [10,15]. Hence, for simplicity, we neglect the FED effects in this paper, by restricting \( m_f \) above to just the ground state for each of the \((n_c, \Omega_z)\) sectors.

We have calculated the spectra using two different methods: 1) We note that \( H_{CL} \) is a single-particle Hamiltonian in each of the sectors \((I0), (I1), (F0) \) and \((F1)\), and can be exactly diagonalized for any \( \Omega_z \) by diagonalizing the corresponding \(((N+1) \times (N+1))\)-dimensional single-particle Hamiltonian matrix. The initial states, i.e. the many-particle ground states \((GS)\) for each \( n_c \), are obtained by filling the single-particle levels in the \( I0 \) and \( I1 \) sectors up to the chemical potential. The final \((n_c = 1)\) many-particle states are obtained by creating particle-hole \((p-h)\) excitations with respect to the corresponding many-particle ground states in the \( F0 \) and \( F1 \) sectors. 2) The PES spectrum is dominated by the single \( p-h \) channel (spectral weight > 95\%) which is calculable³ to very high accuracy even for a dense grid of \( bath \) levels (2). More involved calculations including contributions from all \( p-h \) channels, but limited to using only 21 \( bath \) levels, have also been carried out, and corroborated using the Lanczos recursive algorithm⁴ directly in the many particle Hilbert space. In both cases, as is standard practice, the discrete spectra obtained have been broadened using a Gaussian broadening with \( \sigma \sim 0.1 \) eV. The single and all \( p-h \) spectra are practically identical, and the small missing weight (3–5\%) in the single \( p-h \) channel is visible in the spectra only upon close inspection. Most of the calculations reported in this paper are for model parameters appropriate for the \( La_{1-x}Ba_xMnO_3 \) (LBMO) thin-film samples of Tanaka et al. [6].

Results. – Our results for the doping variation of the PES, obtained at \( T = 0 \) in the fully spin-polarised FM phase \((\Omega_z = 1)\), are shown in fig. 1. Figures 1(a), (b) and (c) show the spectra separately in the two \( n_t \) sectors, and for both single and all \( p-h \) channels, for \( x = 0.1, 0.2, \) and \( 0.3 \). The fully averaged spectrum (fig. 1(d)) thus has a main peak with two shoulders, one on each side, separated by about 6.5 eV \((\sim |U_{dd}|)\) from a high-energy correlation satellite (not shown in fig. 1(d))⁵. As seen in fig. 1(a)-(c), with increasing \( x \) till about 0.3, the main peak intensity decreases, while those of the shoulders (and of the correlation satellite), increase substantially⁶. This is similar to what is seen in the core level PES data in \( La_{1-x}Sr_xMnO_3 \) (LSMO) [5]. In the data on LBMO [6] (where \( x \) is not varied), only the low-energy shoulder is distinguishable. We believe that this is because LBMO has a lower \( x \), for the ferro-insulator (FI) to FM transition

²Using a logarithmic discretization of the band, we have also been able to capture the edge singularities separately in the \( n_t = 0 \) and \( n_t = 1 \) sectors [17] and match them with the theory of Nozieres and DeDominicis based on phase shift analysis [9]. Although with current CL-PES resolutions these singularities are unobservable experimentally, the \( n_t = 0 \) edge shows up as the shoulder. The linear discretization calculations capture the smoothed out features we focus on in our paper with less computational effort [17].

³Our initial and final many-particle states are thus direct products of the occupied single-particle states, with first-quantized wave functions that correspond to Slater determinants. In the spectral calculations, we compute matrix elements involving the overlap of such determinants. For a given discretization of the bath, the all-particle-hole calculations of the spectra are model-exact, and satisfy all the exact sum rules.

⁴We expect that the correlation satellite becomes practically unobservable [5] due to charge transfer effects with the ligands, neglected in the present calculation. Its weight gets transferred to the shoulders, raising their intensity to the observed levels, as confirmed by preliminary model calculations [17].
Fig. 1: (Color online) (a), (b), (c) Calculated core-level PES spectra for LBMO at $T = 0$, in the single $p$-$h$ (SPH) and all $p$-$h$ (APH) channels, for the $n_l = 0$ and $n_l = 1$ sectors and for dopings 0.1, 0.2 and 0.3, respectively. (d) The fully averaged APH spectra for the three dopings (normalised to the main peak), showing only the main peak and the low-energy shoulders.

Fig. 2: (Color online) (a) Magnified view of the $T$ dependence of the calculated spectra for LBMO averaged over the two $n_l$ sectors as well as the core spin angles, in the single $p$-$h$ (SPH) channel for $x = 0.15$. (b) The $T$ dependence of the integrated shoulder intensity in the difference spectrum with respect to the paramagnetic spectrum, compared with $M^2(T)$, the square of the (DMFT derived) magnetization. $M(T)$ is also shown.

(0.05 as opposed to 0.16 in LSMO), and hence [10] a smaller ($E_{JT}/D_0$). In that case the small $T$ dependent changes in the higher energy shoulder, separated only by ~ $E_{JT}$ from the main peak which is rather broad in the experiment, would be harder to distinguish. Since all the mechanisms responsible for the breadth of the main peak are not included in our simplified model, we have simulated this effect using a larger Gaussian broadening, of 0.3 eV. The results, shown in fig. 2(a) confirm our explanation. In contrast, data for $T$-variation of the main peak for the LSMO case is shown in fig. 3, where the higher-energy shoulder is clearly distinguishable despite the same level of broadening.

Figure 2(a) also shows a magnified view of $T$ dependence of the fully averaged spectrum in the single $p$-$h$ channel for $x = 0.15$. Clearly, spectral changes as $T$ increases are similar to the changes as $x$ decreases, as observed in LSMO [5]. In fig. 2(b) we show the $T$ dependence of the integrated shoulder intensity in the difference spectrum with respect to the paramagnetic spectrum, and find that it tracks $M^2(T)$, the square of the magnetization (as calculated using the DMFT), in remarkable agreement with the similar correspondence observed experimentally in LBMO [6]. Such a correspondence is not reproduced by conventional rigid-band or cluster calculations.

Given the simplicity of the Hamiltonian $H_{CL}$ (eq. (4)), all the major features of our calculated spectra can be understood from fairly simple considerations. For the purposes of the ensuing discussions, we ignore the fine distinctions between the local $b$ and $t$ bands and between the bath band and the hybridized $b$ band (their bandwidths are the same). Figures 4 and 5 depict the initial state and two important types of final states in each of the $n_\ell$ sectors in the metallic regime, with the bare bandwidth $D_0 = 1.3$ eV, $E_{JT} = 0.29$ eV. The “$b$” band occupancy ($n_b$) is small and the chemical potential, pinned at $\mu \approx -E_{JT}$, lies close to the effective bottom edge, $D$, of the “$b$” band$^1$.

When $n_c = 0$ (fig. 4), i.e., in the environ of undistorted sites, the local “$b$” level in the initial state ($n_c = 0$) is at zero energy and hybridizes sparingly with the levels near the band edge, as the corresponding hybridization amplitudes are small. Thus the local “$b$” character of the filled levels in the initial state is small. When $n_c = 1$, i.e., the core hole gets created, the local “$b$” level is pulled down by an amount $|U_{pd}| = 6.5$ eV, and becomes substantially occupied in the final GS. The local “$b$” character of the occupied levels in the band is again very small.
initial state \((n_c = 0)\). This further reduces the amount of "b" mixing and hence the local "b" character of the occupied levels in the initial state. When \(n_c = 1\) (fig. 5), the "b" level is at \((U_{dd} + U_{pd}) = -1.5\) eV, much closer to the band edge than in the \(n_t = 0\) sector. Nevertheless, the GS when \(n_c = 1\) still has a substantial occupancy of the local "b" level. Hence, the \(\mu^- \rightarrow \mu^+\) transitions (fig. 5) again have a small intensity in the spectrum. The edge is now at an energy\(^5\) \((U_{dd} + 2U_{pd} + \epsilon_c - 2\mu) = 640.18\) eV, 1.5 eV below the edge in the \(n_t = 0\) sector. Just as in the \(n_t = 0\) sector, the main contribution to the spectrum comes from the \(b \rightarrow \mu^+\) transitions (fig. 5), at energy\(^5\) \((U_{pd} - E_{JT} + \epsilon_c - 2\mu) = 641.39\) eV, hence primarily below the GS-to-GS edge from the \(n_t = 0\) sector. Associated with these edge spectra are edge singularities\(^2\) and tails due to \((\text{multi}) p-h\) excitations, which, when smoothed out with Gaussian broadening to mimic the many sources of broadening present in the experiments, give rise to "peaks" with asymmetric [18] line shapes. In fig. 6, the "peaks" are assigned to the appropriate transitions, and their approximate separations are also shown schematically\(^6\).

As mentioned before, the larger peaks in either sector arise due to transitions from the \(b\) level to unoccupied levels in the band, while the smaller ones, which appear as shoulders on either side of the main peak, arise due to transitions from states just below the Fermi level to unoccupied states above. The spectral weights of the edge spectra, and hence those of the shoulders, depend sensitively on the hybridization parameters which, as has been pointed out before, are strongly \(x\) and \(T\) dependent, where as their locations are primarily determined by the coulomb and Jahn-Teller energy parameters.

While only the contribution from lower Hubbard bands (LHB) have been discussed in this paper, we have also calculated the effects of the upper Hubbard bands (UHB) upon the spectra [17]. The features arising due to transitions to the UHB are small compared to those discussed here, since the UHB is unpopulated in the initial state \((n_c = 0)\), and being far off from the Fermi level, does not hybridize much with occupied LHB states.
As one increases $x$ or decreases $T$, the “$b$” bandwidth increases [10]. However, $\mu$ still remains close to $-E_{JT}$, so that the filling and the local “$b$” character of the occupied band levels near $\mu$ increase in the initial state. Hence, one gets a steady transfer of spectral weight from the features where the local “$b$” level is unoccupied in the final state, to those where it is occupied in the final state, as seen in the bare or un-averaged spectra (figs. 1(a), (b), (c)). The spectra shown in fig. 1(d) are averaged over the contributions from the two $n_\ell$ sectors (and additionally over $\Omega_z$ for figs. 2(a) and (b)), with statistical weights which are themselves functions of $x$ and $T$. The net effect is that the two shoulders on the two sides of the main peak, arising from smoothed out edge spectra as shown above, increase in intensity with increasing $x$ or decreasing $T$, in agreement with experiments. Thus, while the positions of the shoulders are primarily determined by local energetics, the $x$ and $T$ dependence of their spectral weights arises from the same mechanism of bandwidth reduction with decreasing doping and increasing temperature which causes the ferro-metal–para-insulator transitions in manganites, as discussed in detail in refs. [10,15].

In other words the same strong electron-phonon and electron-spin couplings that are responsible for the exotic phenomena observed in manganites including Colossal Magnetoresistance also give rise to the novel doping and temperature dependence of the photoemission spectra.

In our simplified model we have neglected effects of spin-orbit coupling. Hence we have only one main peak in our spectra. Inclusion of this coupling would give rise to two peaks corresponding to $2p_{3/2}$ and $2p_{1/2}$, as seen experimentally, with $x$ and $T$ dependent shoulders appearing around both peaks. However, experimentally the shoulders are not so prominently visible on the $2p_{1/2}$ peak. As already pointed out in the experimental paper [6], this is because of the extra broadening in the $2p_{1/2}$ peak caused by additional decay channels that are not included in our model$^7$.

When comparing our theory with the experimental data, it is important to note that the features that we have focussed on will in reality ride on a broad, largely $T$, $x$ independent background [5,6]. The latter, known to arise from multiplet interactions and charge transfer effects with the ligand, seems to be reasonably well explainable using conventional methods [5,6]. We have not included the multiplet interactions in our work, which is why the overall background shape of our calculated spectra does not resemble the experimental one. Accordingly, for comparison with real data, we have focussed on difference spectra, as in fig. 2, where this background gets subtracted out. Indeed, the relative weight of the prominent lower-energy shoulder in our calculation is about 0.16, which is similar to that of the experimental spectra.

$^7$However, it is easy to mimic this effect by further increasing the size of the broadening used in our calculations, whence the shoulders do indeed become unobservable.

In conclusion, we have presented Mn 2$p$ core-level PES calculations by extending the 2-fluid $f$-$b$ model for manganites [10] that takes into account the simultaneous presence of strong electron-lattice, spin-spin and charge-charge interactions. Our results provide a plausible explanation, we believe for the first time, for the unusual redistribution of spectral weight over several eV upon varying $x$ and $T$, and a correspondence between the effect of increasing $x$ and decreasing $T$, as experimentally observed [5,6].

***

We would like to thank the JNCASR (NP, SSG) and the DST (HRK, PS, DDS) for financial support.

REFERENCES

[1] Jin S. et al., Science, 264 (1994) 413; Chahara K., Ohno T., Kasai M. and Kozono Y., Appl. Phys. Lett., 63 (1993) 1990.
[2] See, e.g., Salamon M. B. and Jaime M., Rev. Mod. Phys., 73 (2001) 583.
[3] Sarma D. D. et al., Phys. Rev. B, 53 (1996) 6873.
[4] Saitoh T. et al., Phys. Rev. B, 56 (1997) 8836.
[5] Horiba K. et al., Phys. Rev. Lett., 93 (2004) 236401.
[6] Tanaka H. et al., Phys. Rev. B, 73 (2006) 094403.
[7] Barman S. R., Chainani A. and Sarma D. D., Phys. Rev. B, 49 (1994) 8475.
[8] Gunnarson O., Schonhammer K., Sarma D. D., Hillebrecht F. U. and Campagna M., Phys. Rev. B, 32 (1985) 5499; Sarma D. D. and Taraphder A., Phys. Rev. B, 39 (1989) 11570.
[9] Ohtaka K. and Tanabe Y., Rev. Mod. Phys., 62 (1990) 929, and references therein.
[10] Ramakrishnan T. V., Krishnamurthy H. R., Hassan S. R. and Venketeswara Pai G., Phys. Rev. Lett., 92 (2004) 157203; cond-mat/0308396; Venketeswara Pai G., Hassan S. R., Krishnamurthy H. R. and Ramakrishnan T. V., Europhys. Lett., 64 (2003) 696.
[11] Georges A., Kotliar G., Krauth W. and Rozenberg M. J., Rev. Mod. Phys., 68 (1996) 13.
[12] Bocquet A. E. et al., Phys. Rev. B, 46 (1992) 3771.
[13] Sarma D. D. et al., Phys. Rev. Lett., 75 (1995) 1126; Satpathy S., Popovic Z. S. and Vukajlovcic F. R., Phys. Rev. Lett., 76 (1996) 960; Mahadevan P., Shanthi N. and Sarma D. D., Phys. Rev. B, 54 (1996) 11199.
[14] Freericks J. K. and Zlatic V., Rev. Mod. Phys., 75 (2003) 1333.
[15] Hassan S. R., PhD Thesis, Indian Institute of Science (2003); Hassan S. R., Krishnamurthy H. R., Venketeswara Pai G. and Ramakrishnan T. V., in preparation.
[16] Kim H. D., Noh H. J., Kim K. H. and Oh S. J., Phys. Rev. Lett., 93 (2004) 126404.
[17] The details will be published elsewhere. See also Prabuddha Sanyal, PhD Thesis (Indian Institute of Science, 2006); Subhra Sen Gupta, PhD Thesis (Indian Institute of Science, 2006).
[18] Doniach S. and Sunji´c M., J. Phys. C, 3 (1970) 285.