Zone Boundary Softening of the Spin-Wave Dispersion in Doped Ferromagnetic Manganites

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We argue that the new distinct features observed in doped ferromagnetic manganites $R_{1-x}D_x\mathrm{MnO_3}$ (RD = LaSr, PrSr, NdSr, and LaCa), the softening of the spin-wave dispersion at the zone boundary and the increase of the spin-wave stiffness constant with x, have purely magnetic spin origin. They indicate the breakdown of the canonical double-exchange limit, and reflect otherwise natural consequence of the e_g-band filling in the half-metallic regime. Details of the realistic electronic structure are important and significantly modify the analysis based on the minimal tight-binding Hamiltonian for e_g electrons. [S0031-9007(99)08820-1]

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The understanding of many fascinating properties of colossal magnetoresistive perovskite manganites $R_{1-x}D_x\mathrm{MnO_3}$ (R = trivalent rare-earth ion, D = divalent ion) circles around two questions [1]: (i) whether the double-exchange (DE) mechanism alone is enough and (if apparently not) (ii) whether a strong Jahn-Teller based electron-lattice coupling is the trigger for the unusual behavior. Recent studies of the spin-wave dispersion (SWD) of doped ferromagnetic (FM) manganites provide a new piece of information, which is typically argued based on these two standpoints. A brief sketch of the current situation is given below. Perring *et al.* [2] measured the SWD of the high Curie temperature ($T_C = 355$ K) system $\mathrm{La_{0.7}Pb_{0.3}MnO_3}$ throughout the Brillouin zone and claimed that a simple Heisenberg Hamiltonian

$$E[\{\mathbf{e}_i\}] = -\frac{1}{2}\sum_{ik} J_k \mathbf{e}_i \cdot \mathbf{e}_{i+k} \qquad (1)$$

(here, $\mathbf{e}_i$ is the direction of magnetic moment at the site i) with solely the nearest-neighbor (nn) coupling J_1 accounts for the entire dispersion relation $\omega(\mathbf{q})$ and also for T_C to within 15%. Furukawa [3] argued that the result seems to be consistent with the DE limit $W/I < 1$ (W being the e_g bandwidth, I being Hund's coupling) of the FM Kondo lattice model (KLM). Similar classification has been ascribed to higher-T_C manganite $\mathrm{La_{1-x}Sr_xMnO_3}$ ($T_C = 378$ K at $x = 0.3$) in the region $0.175 \le x \le 0.3$, the spin dynamics of which was reported to be regular for FM materials [4]. The main controversies came later, when an unexpected softening of the SWD at the zone boundary was observed in several manganites with lower but yet very different T_C: $\mathrm{Pr_{0.63}Sr_{0.37}MnO_3}$ ($T_C = 301$ K) [5], $\mathrm{La_{0.7}Ca_{0.3}MnO_3}$ ($T_C = 242$ K) [6], and $\mathrm{Nd_{0.7}Sr_{0.3}MnO_3}$ ($T_C = 198$ K) [7]. Hwang *et al.* [5] showed that the experimental $\omega(\mathbf{q})$ can be reproduced reasonably well by the Heisenberg Hamiltonian with the parameters (for $\mathrm{Pr_{0.63}Sr_{0.37}MnO_3}$) $J_1 = 10.1$, $J_2 = -0.6$, $J_3 = 0.6$, and $J_4 = 2.7$ meV, thus clearly demonstrating the importance of the long-range FM coupling J_4. They also argued that the next important contribution which improves the fit is J_8 [8]. Even more pronounced softening was observed in the 50% doped manganites $\mathrm{Pr_{0.5}Sr_{0.5}MnO_3}$ and $\mathrm{Nd_{0.5}Sr_{0.5}MnO_3}$, both in the FM state and within FM layers in the A-type antiferromagnetic (AFM) state [9]. These observations gave rise to several scenarios of the low-temperature behavior of doped manganites, among which are the spin-lattice coupling, the orbital ordering, and the precursor of the AFM spin ordering. The purpose of this work is to show that the observed softening of the SWD at the zone boundary is a natural consequence of the e_g band filling in the half-metallic (HM) regime, implying that the canonical DE limit is not appropriate and that neither the lattice deformation nor the orbital ordering are required for the SWD softening. We employ both the tight-binding (TB) analysis and direct adiabatic frozen-spin-spiral calculations of $\omega(\mathbf{q})$ [10] performed for the cubic virtual-crystal alloy $\mathrm{La_{1-x}Ba_xMnO_3}$ within local-spin-density approximation (LSDA).

Our starting point is the fact that the total energy change due to small nonuniform rotations of magnetic moments near an equilibrium, i.e., the processes relevant to the spin-wave excitations, can be exactly mapped onto the Heisenberg model (1) [11,12]. If the magnetic part of an effective one-electron potential is described solely by the on-site exchange splitting $\hat{\Delta}_{\mathrm{ex}}$ between the majority-spin (↑) and the minority-spin (↓) states [13], the parameters J_k can be found as

$$J_k = \frac{1}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\mathrm{Tr}_L\{\hat{\Delta}^0_{\mathrm{ex}}\hat{G}^{\uparrow}_{0k}(\varepsilon)\hat{\Delta}^k_{\mathrm{ex}}\hat{G}^{\downarrow}_{k0}(\varepsilon)\}, \qquad (2)$$

where $\hat{G}^{\uparrow,\downarrow}$ is the one-electron Green function in the real space, and Tr_L denotes the trace over the orbital indices $\{L\}$. First, we discuss several basic features of magnetic interactions (2) for HM ferromagnets. Consider the TB Hamiltonian $\hat{\mathcal{H}}^{\sigma} = -\hat{t} + \Delta_{\mathrm{ex}}\hat{1}\delta_{\sigma\downarrow}$, where $\hat{t} = \|t_{ij}^{LL'}\|$

is the matrix of kinetic hoppings between nn orbitals and $\hat{1} = \|\delta_{LL'}\delta_{ij}\|$ is the unity matrix in the subspace spanned by orbital and site indices. Assume that $\Delta_{\rm ex}$ is the largest parameter in the problem and expand $\hat{G}^{\downarrow}(\varepsilon) = (\varepsilon\hat{1} - \hat{\mathcal{H}}^{\downarrow})^{-1}$ in the occupied part of the spectra $\varepsilon \le \varepsilon_F$ up to the 2nd order of $(\varepsilon\hat{1} + \hat{t})/\Delta_{\rm ex}$: $\hat{G}^{\downarrow}(\varepsilon) \simeq -\hat{1}/\Delta_{\rm ex} - (\varepsilon\hat{1} + \hat{t})/\Delta_{\rm ex}^2 - (\varepsilon\hat{1} + \hat{t})^2/\Delta_{\rm ex}^3$. Then, for the nn coupling we have $J_1 \simeq J_1^D + J_1^S$, where

$$J_1^D = -\frac{1}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\mathrm{Tr}_L\{\hat{G}_{01}^{\uparrow}(\varepsilon)\hat{t}_{10}\} \qquad (3)$$

is the DE contribution (a 1st order effect), and

$$J_1^S = -\frac{1}{\pi\Delta_{\rm ex}}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\mathrm{Tr}_L\{\varepsilon\hat{G}_{01}^{\uparrow}(\varepsilon)\hat{t}_{10}\} \qquad (4)$$

is the superexchange (SE) contribution (a 2nd order effect). The same 2nd order term in the expansion leads to the longer-range coupling,

$$J_k = -\frac{1}{2\pi\Delta_{\rm ex}}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\mathrm{Tr}_L\{\hat{G}_{0k}^{\uparrow}(\varepsilon)\,(\hat{t})_{k0}^2\}, \qquad (5)$$

where $(\hat{t})_{k0}^2 = \sum_j \hat{t}_{kj}\hat{t}_{j0}$. For the one-dimensional one-band TB model these coupling parameters can be expressed analytically [14]. In Fig. 1 we show results for a more realistic two-band model on a cubic lattice, where the hoppings between nn e_g orbitals have been parametrized in terms of the $dd\sigma$ Slater-Koster integral [15] [note that $W = 6|(dd\sigma)|$]. To be close to the LSDA picture, we adopt the Stoner-type splitting $\Delta_{\rm ex} = I(4 - x)$. The main conclusions will also hold for the FM KLM, which is based on a slightly different definition of $\Delta_{\rm ex}$ [13]. We note the following.

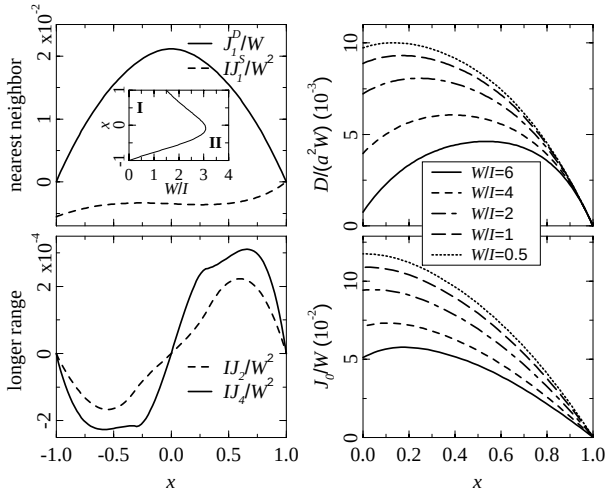

FIG. 1. Two-band $dd\sigma$ model on a cubic lattice with the Stoner-type intra-atomic exchange splitting $\Delta_{\rm ex} = I(4 - x)$. Left panel: leading interatomic interactions obtained from the $1/\Delta_{\rm ex}$ expansion. The inset shows the equation of states: $J_1^D(W_C, x) = -2J_1^S(W_C, x)$ (see text). Right panel: spin-wave stiffness constant (D) and $J_0 = \sum_k J_k$, calculated in the same manner as in Ref. [10]. Only HM solutions are shown.

(i) The ferromagnetic interaction $J_1^D(x)$ has a maximum at $x = 0$, and vanishes at $x = \pm 1$ (↑-spin band edges). On the contrary, the intercation J_1^S is antiferromagnetic. $|J_1^S(x)|$ decreases nearly monotonously with x. At $x = -1$ (filled ↑-spin band) we obtain the standard limit for the SE interaction in the half-filled insulating state: $J_1(-1) \equiv J_1^S(-1) = -(dd\sigma)^2/\Delta_{\rm ex}$. The behavior of the total nn exchange J_1 is determined by these two competing factors. Such a simple analysis can be very instructive for the understanding of the W dependence of J_1. Indeed, from $dJ_1/dW = 0$ we obtain the following equation of states: $J_1^D(W_C, x) = -2J_1^S(W_C, x)$. If $W < W_C$, the W dependence of J_1 is governed by the FM DE interaction J_1^D and $dJ_1/dW > 0$ (region I in the inset of Fig. 1). If $W > W_C$, the W dependence of J_1 is governed by the AFM SE interaction J_1^S and $dJ_1/dW < 0$ (region II). The critical value W_C depends on x. The upper limit of W_C, which takes place near $x = 0$, can be estimated as $W_C/I < 3.1$. Since $I \le 1$ eV [13], we have $W_C \le 3.1$ eV. For the FM manganites, the first-principles band calculations yield $W > 3$ eV [16]. Thus, the overall picture suggested by such calculations is far from the DE limit, and corresponds either to the critical behavior with $W \approx W_C$ or to the SE regime.

(ii) The hole doping ($x > 0$) gives rise to the longer-range FM interactions J_2 and J_4, which vanish in the undoped case $x = 0$. These interactions compensate the reduction in the nn FM DE coupling in the small-$\mathbf{q}$ regime [thus contributing to the spin-wave stiffness constant $D = \frac{1}{6}\nabla_{\mathbf{q}}^2\omega(\mathbf{q})|_{\mathbf{q}=0}$], and also give rise to the softening of the SWD at the zone boundary. The validity of this scenario can be checked experimentally if the electron doping ($x < 0$) is possible. The present analysis suggests AFM longer-range interactions in the electron doping regime, which should result in the "hardening" of the SWD at the zone boundary.

To conclude this model part, we would like to comment on the current classification of the FM manganites. (i) The increase of D with x observed in $La_{1-x}Sr_xMnO_3$ for $0.175 \le x \le 0.3$ [4] cannot be ascribed to the DE mechanism, but may be caused by the contribution from longer-range FM interactions (particularly J_4) in the regime $W/I > 2$ (Fig. 1). (ii) The FM band structure is a good starting point for the analysis of the low-temperature SWD, but not for T_C. Except for a small region near $x = 0$, the mean-field Curie temperature $T_C^{\rm MF} = J_0/3k_B$ is a decreasing function of x for all physically meaningful ratios W/I if $J_0 = \sum_k J_k$ is evaluated in the FM ground state (Fig. 1), in straight contrast to the experimental finding for $La_{1-x}Sr_xMnO_3$ [17]. In this context, the observation that the same Heisenberg Hamiltonian explains both the low-temperature SWD and the T_C in $La_{0.7}Pb_{0.3}MnO_3$ [2] is probably fortuitous.

The conclusions remain valid if D and $T_C^{\rm MF}$ are calculated using a more realistic LSDA band structure [10] (Fig. 2). At larger lattice constants a, where the

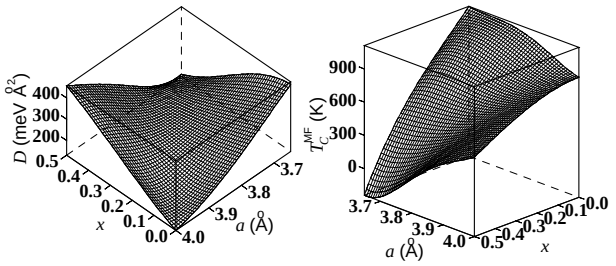

FIG. 2. Spin-wave stiffness constant and mean-field Curie temperature $T_C^{\mathrm{MF}} = (1/3k_B)\sum_k J_k$ for the Heisenberg Hamiltonian derived near the FM ground state in $La_{1-x}Ba_xMnO_3$.

system is in the HM regime, D increases with x. As will be discussed later, the deviation from the HM behavior at smaller a may significantly modify results of the simple TB analysis for D. However, this should not be the case for $La_{1-x}Sr_xMnO_3$, which is known to be a good candidate for the normal HM behavior [18]. Then, the experimental trend $D(x)$ suggests that longer-range FM interactions play important roles also in this compound, and the SWD (if measured throughout the Brillouin zone) should exhibit the softening at the zone boundary, similar to other manganites [5–7]. The simple nn Heisenberg character of the SWD reported for $La_{0.7}Pb_{0.3}MnO_3$ [2] remains to be enigmatic. From our point of view, it is unlikely that the canonical DE limit $W/I < 1$ [3] is regained in this particular compound. Additional information about the x and/or pressure dependence of the SWD could clarify the situation.

The simple TB model captures the essential points of the problem, though some additional ingredients of the realistic band structure may modify the analysis quantitatively. For example, using $I = 0.8$–1.0 eV [13] and the experimental coupling $J_4 = 2.7$ meV [5], W can be estimated from the TB picture (Fig. 1) as 2.9–3.2 eV. With these I and W, the nn coupling $J_1 \simeq J_1^D + J_1^S$ can be further estimated as 14.3–20.7 meV, being substantially larger than the experimental value 10.1 meV. The difference is primarily due to the nn AFM SE interactions between t_{2g} orbitals, which are missing in our TB model. The analysis based on the LSDA suggests that the relative strength of the AFM and FM nn interactions associated correspondingly with the t_{2g} and e_g states in the hypothetical cubic $LaMnO_3$ (the experimental volume, $a = 3.934$ Å) is characterized by the ratio $\sim 1/3$ [19].

Another discrepancy is more subtle. Although in the perturbative TB analysis J_2 is considerably suppressed in comparison with J_4 due to peculiarities of hoppings between nn e_g orbitals (for comparison, $|J_4| < |J_2|$ in the one-band KLM [3]), it remains to be positive for $x > 0$. One can expect, however, that the itinerant O($2p$) band plays important roles. Since the Mn($3d$)-O($2p$) energy separation is finite and comparable with Δ_{ex} (Fig. 3), the O($2p$) states cannot be easily eliminated from the

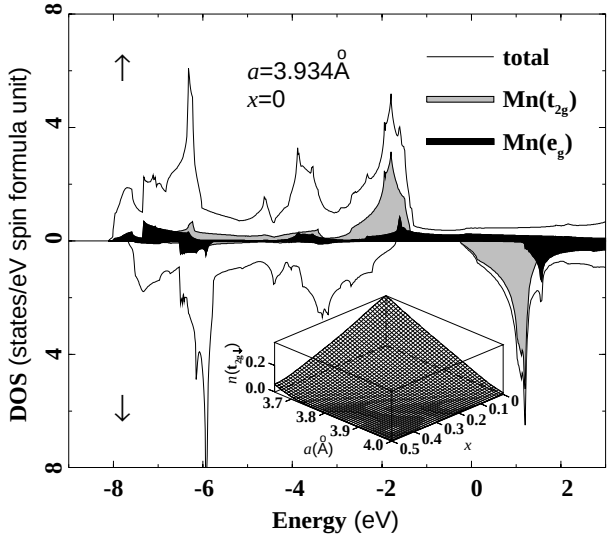

FIG. 3. Total and partial densities of states for cubic FM $LaMnO_3$. The Fermi energy is at zero. The inset shows the population of the ↓-spin t_{2g} band in $La_{1-x}Ba_xMnO_3$ as a function of x and a.

analysis of magnetic interactions [16,20]. Indeed, the sign problem of J_2 is resolved in the LSDA calculations ($J_2 < 0$ in Fig. 4). Another impact of the O($2p$) band is the existence of extremely long-range magnetic interactions which can spread up to the 15th nearest neighbors (Fig. 4). It is interesting, however, that only the following interactions exhibit an appreciable x dependence: J_1, J_4, J_8, and J_{15}. All of them are confined within the linear ...-Mn-O-Mn-... chains parallel to the $[1,0,0]$ or $[0,1,0]$

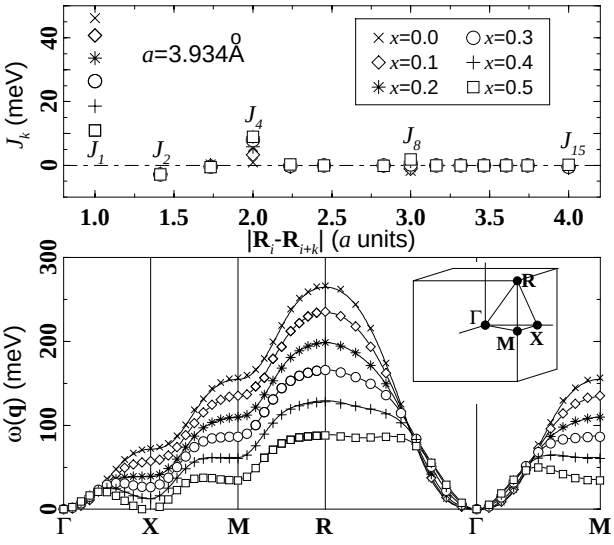

FIG. 4. SWD in $La_{1-x}Ba_xMnO_3$. The first 15 real-space parameters $\{J_k\}$, whose distance dependence is shown in the upper panel, have been Fourier transformed from the calculated $\omega(\mathbf{q})$ (shown by symbols)—see Ref. [10]. SWD curves for the Heisenberg Hamiltonian including these 15 nn interactions are shown by solid lines.

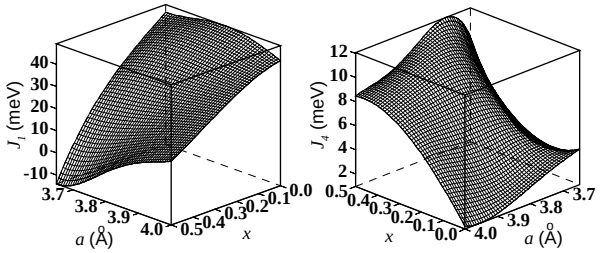

FIG. 5. Two strongest interactions in $La_{1-x}Ba_xMnO_3$.

or $[0, 0, 1]$ direction of the cube [8]. With an increase of x, the interaction(s) J_1 (J_4, J_8, and J_{15}) decreases (increase) as seen in Figs. 4 and 5, resulting in the SWD softening, very similar to the experimental finding [5–7].

Finally, we discuss some possible roles of t_{2g} orbitals. One obvious contribution is the AFM SE interactions in the half-filled t_{2g} band which additionally reduce J_1. Another aspect is related with possible deviation of real materials from the HM regime. The most probable scenario suggested by the LSDA calculations consists in the partial occupation of the $t_{2g\downarrow}$ band by $n(t_{2g\downarrow})$ electrons which would go into the $e_{g\uparrow}$ band in the normal HM regime (Fig. 3). Since in the cubic lattice, the nn hoppings between t_{2g} and e_g orbitals are forbidden [15], the situation may be regarded as the coexistence of two HM systems which exchange electrons with each other. As the population of the e_g band decreases due to self-doping, the strength of the DE and SE e_g interactions will also decrease (Fig. 1). The undoped hypothetical FM $LaMnO_3$ is characterized by a finite $n(t_{2g\downarrow})$ for all considered lattice parameters, resulting in a finite coupling J_4 even at $x = 0$ (Fig. 5). The occupation of the $t_{2g\downarrow}$ band will reduce the SE interaction and give rise to the new FM DE interaction associated with the t_{2g} degrees of freedom. Since the deviation from half-filling results in a rapid increase of the DE component ($\sim |t| n(t_{2g\downarrow})/2$, suggested by the one-dimensional TB model—Ref. [14]), the population of the $t_{2g\downarrow}$ band will be generally favorable for the FM coupling, which is manifested in extra-large values of J_1 obtained for small x and a (Fig. 5), i.e., in the region where $n(t_{2g\downarrow})$ is the largest. $n(t_{2g\downarrow})$ depends on a and x, and is an extra factor which may interfere in the behavior of magnetic interactions. Consider the x dependence of D (Fig. 2). At larger a, where $La_{1-x}Ba_xMnO_3$ exhibits nearly HM behavior (Fig. 3), D increases with x, as expected from the (e_g only) TB model for large ratios W/I (Fig. 1). The region of smaller lattice constants is characterized by an appreciable population $n(t_{2g\downarrow})$, which decreases with x. Then, the x dependence of magnetic interactions in this region is substantially modified by the change of the DE interaction contributed by t_{2g} electrons, and D may decrease with x despite an even larger ratio W/I. Thus, if the system is not in the HM regime, the role of the t_{2g} orbitals becomes more complex.

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