Magnetic Spin Origin of the Charge-Ordered Phase in Manganites

I. V. Solovyev[1,2] and K. Terakura[3,4]
[1]*JRCAT-Angstrom Technology Partnership, 1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan*
[2]*Institute of Metal Physics, Russian Academy of Sciences, Ekaterinburg GSP-170, Russia*
[3]*JRCAT-NAIR, 1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, Japan*
[4]*Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8558, Japan*
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We argue that the charge ordering observed in 50% doped manganites is a manifestation of the peculiar antiferromagnetic spin ordering. The latter, combined with the large Hund's rule physics in manganites, divides the whole system into the quasi-one-dimensional zigzag objects, which exhibit a very unique electronic structure and behave as band insulators. This results in a strong anisotropy of short-range double-exchange interactions, which is responsible for the local stability of the antiferromagnetic state.

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"Charge ordering" is one of the most intriguing phenomena observed in perovskite manganites [1]. Canonical examples of the "charge-ordered" (CO) compounds are some three-dimensional (3D) $R_{1-x}D_x\mathrm{MnO}_3$ [1] and two-dimensional (2D) $R_{1-x}D_{1+x}\mathrm{MnO}_4$ [2,3] manganites ($R =$ trivalent rare-earth ion; $D =$ divalent ion) near $x = 1/2$. If the charge disproportionation took place, these materials would be the best candidates to obtain the equal concentration of $\mathrm{Mn}^{3+}(A)$ and $\mathrm{Mn}^{4+}(B)$ ions, which could then be arranged in the chessboard order (Fig. 1) to optimize the electrostatic energy [4]. Recent experimental data for $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ [5] shed a new light on the origin of the CO state, which cannot be easily reconciled with the simple electrostatic picture: for commensurate carrier concentrations in the higher doping range $x > 0.5$ the system tends to form the very stable one-dimensional (1D) objects—the CO stripes.

There is significant experimental evidence for the existence of a fundamental connection between the CO phenomena and very peculiar forms of the antiferromagnetic (AFM) spin ordering. This was suggested, e.g., by elastic neutron scattering measurements [2] and by the collapse of the CO state in external magnetic fields [6]. Some manganites exhibit the temperature-induced phase transition from the AFM CO state to the ferromagnetic (FM) state (sometimes *A*-type AFM state), accompanied by the disappearance of the charge ordering [1]. Another possible scenario is the direct AFM-to-paramagnetic transition, for which the Néel temperature (T_N) is always lower than the charge ordering temperature. At present, it is not clear whether the charge ordering above T_N (which is accompanied by the orbital ordering [3]) persists independently or is driven by AFM fluctuations of a proper type.

The mechanism of the charge/spin ordering in manganites is not at all clear. After a long time since the pioneering work of Goodenough [4], who predicted the correct magnetic structure for $\mathrm{La}_{1/2}\mathrm{Ca}_{1/2}\mathrm{MnO}_3$ being based on excellent intuition, the problem was addressed again only recently. Different authors emphasized the importance of several ingredients: on-site Coulomb interactions [7–9], the Jahn-Teller distortion (JTD) [9–11], and intersite Coulomb interactions [8,12]. In the present Letter we will argue that the trigger for the charge ordering lies in the unique insulating feature of the quasi-1D FM zigzag chain, the magnetic building block of the CO phase, and is caused by peculiarities of the kinetic e_g hoppings. We will show that the CO phase is stabilized due to the anisotropy of short-range double-exchange (DE) interactions, associated with particular form of the AFM ordering. This is in line with the recent publications [13], which strongly advocate the importance of the DE anisotropy in the physics of manganites. We will demonstrate that the idea is indeed very deep and can be extended even to the CO phase. As the result, the basic properties of the CO state can be described by a simple, analytically solvable model.

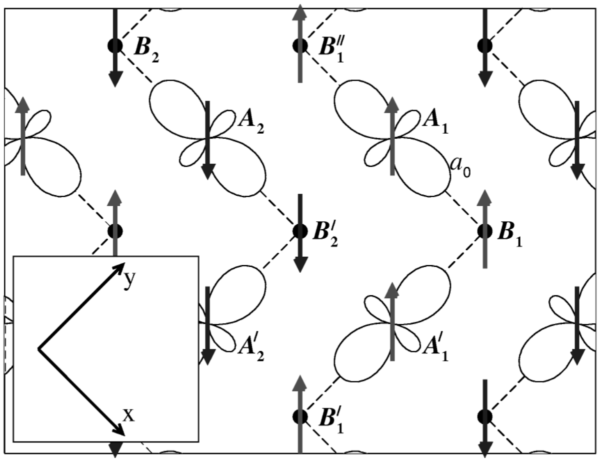

FIG. 1. Spin, orbital, and "charge" ordering in the *a*-*b* planes of 50% doped CO manganites: symbols A and A' stand for Mn^{3+} sites, symbols B, B', and B'' stand for Mn^{4+} sites, and atoms belonging to two neighboring zigzag chains are denoted by the subscripts 1 and 2. $a_0 \equiv |A_1B_1|$ is the lattice parameter for the homogeneous pattern.

The effective one-electron Hamiltonian for spin $\sigma = \uparrow$ or $\downarrow$, which picks up the essence of the e_g-band structure dependence on the magnetic structure is given by (see, e.g., Ref. [13])

$$(\widehat{\mathcal{H}}^{\sigma})_{ij}^{LL'} = -t_{ij}^{LL'} + \Delta_{\mathrm{ex}}(1 - \delta_{e_i\sigma})\delta_{ij}\delta_{LL'}, \qquad (1)$$

where the first term stands for the kinetic $dd\sigma$-type hoppings between nearest-neighbor (nn) e_g orbitals specified by L and L' [14], the second term describes the on-site spin exchange splitting of the e_g levels, and e_i is the direction of magnetic moment at the site i ($e_i = \uparrow$ or $\downarrow$). It is implied that Δ_{ex} is driven by the large Hund's rule coupling in manganites. The remaining ingredients of our model, the nn AFM superexchange (SE) interaction J^S, the local orbital splitting of e_g levels at A sites Δ_{O} (which may be caused by electron-electron or/and electron-lattice interactions [15]), and a parameter controlling the charge inhomogeneity Δ_{C}, will be specified later.

The spin ordering in the a-b plane of the CO phase is shown in Fig. 1. It is formed by 1D FM zigzag chains (e.g., 1 and 2), propagating in the $[\bar{1}, 1, 0]$ direction and being antiferromagnetically coupled in the $[1, 1, 0]$ directions. For the 2D manganites, this is exactly the structure to be addressed. In the 3D case, the 2D structure shown in Fig. 1 is periodically repeated in the $[0, 0, 1]$ (c) direction with the AFM alternation of the directions of magnetic moments, resulting in the so-called *CE* structure [4]. For example, in the nearest neighborhood along the c direction of the chain 1 will be the chain (say, 3) with the reversed moments, etc.

Consider these magnetic structures in the DE limit $\Delta_{\mathrm{ex}} \to \infty$. Large Δ_{ex} suppresses the electron hoppings between all neighboring zigzag chains. Thus, as the first approximation, the chains become decoupled from each other, and may be regarded as the building blocks of the CO manganites, both in the 2D and 3D cases. For a single chain, the Hamiltonian (1) can be diagonalized analytically. For these purposes, it is convenient to adopt the following basis at the four nonequivalent sites [16]:

$$\begin{aligned} A, B:&\ \ |1\rangle = |3x^2 - r^2\rangle,\ |2\rangle = |y^2 - z^2\rangle \\ A', B':&\ \ |1\rangle = |3y^2 - r^2\rangle,\ |2\rangle = |x^2 - z^2\rangle. \end{aligned} \qquad (2)$$

At the sites A and A', the choice is dictated by the geometry of the zigzag chain. The basis at the corner sites can be taken in the form B or B' rather arbitrarily. For the sake of convenience, these two types have been assigned to the atoms in the a-b plane as shown in Fig. 1. For the 3D systems, the basis is repeated in the c direction. In this basis, the nonvanishing hoppings in the chain take the form: $t_{AB}^{11} = t_{A'B'}^{11} = 1$, $t_{AB''}^{11} = t_{A'B}^{11} = -\frac{1}{2}$, and $t_{AB''}^{12} = t_{A'B}^{12} = \frac{\sqrt{3}}{2}$ [note also that $t_{ij}^{LL'} = t_{ji}^{L'L}$, the sites B' and B'' are equivalent, and all energies throughout the paper are in units of the transfer integral $(dd\sigma)$ [14]]. The periodicity of these hopping matrix elements is characterized by the minimal translation $\mathbf{R}_0 = [\bar{a}_0, a_0, 0]$, which connects the sites A and A'. Then, we can apply the generalized Bloch transformation [17]. This gives the 4×4 Hamiltonian, for the chain 1 and the spin $\sigma = \uparrow$ (the basis is in the following order: the states 1, 2 of A sites, then the states 1, 2 of B sites),

$$\hat{H}(k) = \begin{pmatrix} 0 & 0 & \frac{1}{2}e^{-ik} - 1 & -\frac{\sqrt{3}}{2}e^{-ik} \\ 0 & \Delta_{\mathrm{O}} & 0 & 0 \\ \frac{1}{2}e^{ik} - 1 & 0 & \Delta_{\mathrm{C}} & 0 \\ -\frac{\sqrt{3}}{2}e^{ik} & 0 & 0 & \Delta_{\mathrm{C}} \end{pmatrix}, \qquad (3)$$

where $-\pi \leq k \leq \pi$. Δ_{O} controls the orbital splitting of e_g levels at A sites, Δ_{C} controls the charge distribution between A and B sites, so that at sites A and A' the orbitals $|1\rangle$ are preferentially occupied, while at sites B and B' both orbitals $|1\rangle$ and $|2\rangle$ are equally occupied. The Hamiltonian has the following eigenvalues: $\varepsilon_{\pm}(k) = \frac{1}{2}(\Delta_{\mathrm{C}} \pm \sqrt{\Delta_{\mathrm{C}}^2 + 8 - 4\cos k})$, the bonding and antibonding states; $\varepsilon_A = \Delta_{\mathrm{O}}$, the nonbonding $y^2 - z^2/x^2 - z^2$ atomic orbitals at A sites; and $\varepsilon_B = \Delta_{\mathrm{C}}$, a nonbonding combination of orbitals belonging to different B sites. The splitting into the bonding, nonbonding, and antibonding states is clearly seen in the band calculations [10]. The lowest energy part of the spectrum is formed by the single band $\varepsilon_{-}(k)$, which is well separated from the rest of the eigenvalues [18]. In the CO regime, when there is exactly one electron per two sites, A and B, the band $\varepsilon_{-}(k)$ is fully occupied. This yields an insulating behavior with the gap $\min[\varepsilon_A, \varepsilon_B] - \varepsilon_{-}(0)$. This is the very important feature of the electronic structure of the isolated zigzag chain, whose origin is related with peculiarities of the kinetic e_g hoppings. $\varepsilon_{-}(k)$ does not depend on the orbital splitting Δ_{O}. Thus, for the isolated chain, the $(3x^2 - r^2/3y^2 - r^2)$-type orbital ordering [3] (shown in Fig. 1) is entirely determined by the kinetic effects.

Let us turn to the local stability of the peculiar AFM ordering with respect to nonuniform rotations of magnetic moments near the AFM equilibrium. The problem is formulated in terms of the magnetic interactions [19],

$$J_{ij} = \frac{\Delta_{\mathrm{ex}}^2}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\, \mathrm{Tr}_L\{\hat{\mathcal{G}}_{ij}^{\uparrow}(\varepsilon)\hat{\mathcal{G}}_{ji}^{\downarrow}(\varepsilon)\}, \qquad (4)$$

where $\hat{\mathcal{G}}^{\sigma}(\varepsilon) = (\varepsilon - \widehat{\mathcal{H}}^{\sigma})^{-1}$ is the Green function (GF) in the real space, the Hamiltonian $\widehat{\mathcal{H}}^{\sigma}$ is given by Eq. (1) and may also include Δ_{C} and Δ_{O} in the same manner as in Eq. (3), and Tr_L denotes the trace over the orbital indices. Our goal is to find J_{ij} in the DE limit $\Delta_{\mathrm{ex}} \to \infty$. For the nn interactions in the FM chain, this yields [20]

$$J_{A_1B_1}^{D} = -\frac{1}{2\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} d\varepsilon\, G_{A_1B_1}^{11}(\varepsilon)t_{B_1A_1}^{11}, \qquad (5)$$

where $\hat{G}(\varepsilon)$ is the GF for the Hamiltonian (3) in the real space, which can be treated analytically. This gives

$$J_{A_1B_1}^{D}(\Delta_{\mathrm{C}}) = \frac{1}{4\pi}\int_0^{\pi} dk\, \frac{2 - \cos k}{\sqrt{\Delta_{\mathrm{C}}^2 + 8 - 4\cos k}}, \qquad (6)$$

whence it immediately follows $\frac{d}{d\Delta_C} J^D_{A_1B_1}(\Delta_C) < 0$, suggesting that the charge inhomogeneity tends to destroy the intrachain ferromagnetism and that the charge ordering itself cannot be the driving force of the peculiar AFM zigzag ordering in the CO manganites.

In the following, we consider only homogeneous solutions corresponding to $\Delta_C = 0$ and argue that the anisotropy of the AFM ordering is the key to the local stability of the zigzag structure. First, the AFM zigzag ordering additionally stabilizes the FM coupling within the chain. Indeed, for $\Delta_C = 0$ we obtain $J^D_{A_1B_1} \equiv J^D_{A_1B_1}(0) \simeq 0.174$, being substantially larger than $J^D_{2D} \simeq 0.115$, the nn DE coupling in the homogeneous 2D FM plane with $x = 0.5$.

In order to calculate the interchain interactions, we shall find the GF elements, $\hat{\mathcal{G}}^{\uparrow}_{ij}$ and $\hat{\mathcal{G}}^{\downarrow}_{ji}$, between sites belonging to neighboring zigzag chains with opposite directions of magnetic moments (e.g., $i \in 1$ and $j \in 2$ for the interactions between chains 1 and 2 in Fig. 1). For these purposes we use separate chains as the reference system, include the hopping matrix elements between the chains as a perturbation, $\hat{\mathcal{G}}^{\uparrow}_{ij}(\varepsilon) = -\sum_{l\in 1, m\in 2} \hat{G}_{il}(\varepsilon)\hat{t}_{lm}\hat{G}_{mj}(\varepsilon - \Delta_{\text{ex}})$ and $\hat{\mathcal{G}}^{\downarrow}_{ji}(\varepsilon) = -\sum_{m\in 2, l\in 1} \hat{G}_{jm}(\varepsilon)\hat{t}_{ml}\hat{G}_{li}(\varepsilon - \Delta_{\text{ex}})$, and employ the asymptotic behavior $G^{LL'}_{mj}(\varepsilon - \Delta_{\text{ex}}) \simeq -1/\Delta_{\text{ex}}\delta_{mj}\delta_{LL'}$ in the occupied part of the spectra $\varepsilon \le \varepsilon_F$ when $\Delta_{\text{ex}} \to \infty$. We consider only nn interactions [21]. All matrix elements of $\hat{\mathcal{G}}^{\sigma}(\varepsilon)$ obtained in such a manner and relevant to the in-plane and interplane nn interactions are collected in Table I.

For the in-plane interactions between sites A_1 and B'_2, we obtain from Eq. (4)

$$J^D_{A_1B'_2} = \frac{1}{16\pi} \operatorname{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \times \{2G^{11}_{A_1A_1}(\varepsilon) - G^{11}_{A_1A'_1}(\varepsilon) + 6G^{22}_{A_1A_1}(\varepsilon)\} \times G^{11}_{B_1B_1}(\varepsilon).$$

The substitution of the GF elements yields

$$J^D_{A_1B'_2}(\Delta_O) = J^D_{A_1B'_2}(0) - \frac{3\Delta_O}{64\pi} \int_0^{\pi} dk \, \frac{5 - 4\cos k}{f_k^3(\Delta_O + f_k)},$$

where $f_k = \sqrt{2 - \cos k}$ and $J^D_{A_1B'_2}(0) \simeq 0.106$.

Then, we note that besides the anisotropic nn DE interactions, $J^D_{A_1B_1}$ and $J^D_{A_1B'_2}$, there are also the SE AFM nn interactions J^S, which we assume to be isotropic. Formally, J^S can be obtained in the first order of $1/\Delta_{\text{ex}}$ expansion for nn magnetic interactions [20]. Under this general definition, J^S may be regarded as a combination of SE interactions associated with both t_{2g} and e_g degrees of freedom. Then, the 2D AFM zigzag structure will be stable if

$$J^D_{A_1B'_2}(\Delta_O) < |J^S| < J^D_{A_1B_1} \tag{7}$$

(i.e., when the total coupling $J^D + J^S$ remains FM in the chain, and becomes AFM between the chains). Since $J^D_{A_1B'_2}(0) < J^D_{A_1B_1}$, the 2D AFM zigzag ordering may be stabilized due to the anisotropy of the DE interactions alone, without an additional orbital splitting of e_g levels at A sites. The finite splitting Δ_O significantly increases the stability area (Fig. 2). The anisotropy of magnetic interactions is clearly seen in band calculations [11], though the AFM counterpart J^S obtained in the *ab initio* manner seems to be insufficient to stabilize the AFM coupling between the chains and a small JTD becomes indispensable. If $J^D_{A_1B'_2}(\Delta_O) > |J^S|$ ($|J^S| > J^D_{A_1B_1}$) the 2D AFM zigzag ordering becomes unstable with respect to the homogeneous FM (bipartite AFM) ordering.

TABLE I. The Green function elements relevant to nn interchain exchange interactions in the a-b plane ($ij = A_1B'_2$) and between neighboring a-b planes ($ij = X_1X_3$, where $X = A$ or B). Remaining elements are either zeros or appear in Eq. (4) in the combination with a zero element. The hopping matrix elements are $t^{11}_{A_1B'_2} = -\frac{1}{2}$, $t^{21}_{A_1B'_2} = \frac{\sqrt{3}}{2}$, $t^{11}_{A'_1B'_2} = \frac{1}{4}$, $t^{11}_{X_1X_3} = \frac{1}{4}$, $t^{12}_{X_1X_3} = t^{21}_{X_1X_3} = \frac{\sqrt{3}}{4}$, and $t^{22}_{X_1X_3} = \frac{3}{4}$. Note also the symmetry properties: $t^{LL'}_{ij} = t^{L'L}_{ji}$, $G^{11}_{B'_2B'_2} = G^{11}_{B_1B_1}$, and $G^{LL}_{X_3X_3} = G^{LL}_{X_1X_1}$.

ij	LL'	$\Delta_{\text{ex}}(\hat{\mathcal{G}}^{\uparrow})^{LL'}_{ij}$	$\Delta_{\text{ex}}(\hat{\mathcal{G}}^{\downarrow})^{L'L}_{ji}$
$A_1B'_2$	11	$G^{11}_{A_1A_1}t^{11}_{A_1B'_2} + G^{11}_{A_1A'_1}t^{11}_{A'_1B'_2}$	$G^{11}_{B'_2B'_2}t^{11}_{B'_2A_1}$
$A_1B'_2$	21	$G^{22}_{A_1A_1}t^{21}_{A_1B'_2}$	$G^{11}_{B'_2B'_2}t^{12}_{B'_2A_1}$
X_1X_3	LL'	$G^{LL}_{X_1X_1}t^{LL'}_{X_1X_3}$	$G^{L'L'}_{X_3X_3}t^{L'L}_{X_3X_1}$

In the 3D case, the nn interactions along the c direction take the following form ($X = A$ or B; see Table I):

$$J^D_{X_1X_3} = \frac{1}{32\pi} \operatorname{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \{G^{11}_{X_1X_1}(\varepsilon) + 3G^{22}_{X_1X_1}(\varepsilon)\}^2. \tag{8}$$

For A sites this yields

$$J^D_{A_1A_3}(\Delta_O) = J^D_{A_1A_3}(0) - \frac{3\Delta_O}{32\pi} \int_0^{\pi} \frac{dk}{f_k(\Delta_O + f_k)},$$

where $J^D_{A_1A_3}(0) \simeq 0.076$. Then, one can verify that $J^D_{A_1B'_2}(\Delta_O) > J^D_{A_1A_3}(\Delta_O)$. Thus, any J^S which stabilizes

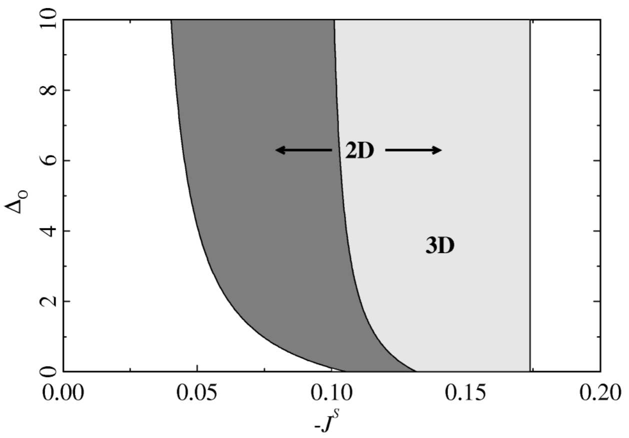

FIG. 2. The parameter range corresponding to the local stability of the AFM zigzag ordering at 50% doping in the 2D case (the full shaded area, both dark and light) and in the 3D cases, the so-called *CE*-type ordering (the light shaded area).

the AFM interchain coupling within the *a*-*b* plane will also stabilize the AFM coupling between A sites along the c direction. The situation for B sites is more complicated. Using Eq. (8) we obtain $J^D_{B_1B_3} \simeq 0.188$, which does not depend on $\Delta_{\rm O}$ and is greater than the in-chain interaction $J^D_{A_1B_1}$. Thus, a sufficiently strong SE interaction $|J^S| > J^D_{B_1B_3}$, which would lead to the total AFM coupling between the sites B_1 and B_3, will also overcome the FM DE interaction within the chain, and make the whole *CE* spin structure unstable with respect to the 3D bipartite AFM (the so-called G-type) ordering. Nevertheless, the 3D *CE* ordering can exist with a joint effect of several interactions in the system, when the total coupling between the sites B_1 and B_3 remains to be FM and the AFM alignment between the planes is driven by other interactions. The criterion is given by the superposition of the three conditions: (i) The 2D AFM zigzag structure is stable—Eq. (7). (ii) The total coupling between neighboring zigzag chains along the c direction is AFM,

$$2|J^S| > J^D_{A_1A_3}(\Delta_{\rm O}) + J^D_{B_1B_3}\,. \tag{9}$$

(iii) The sum of all Heisenberg-type interactions in the *CE* structure in which the B_1 site is involved, $\sum_i (J^D_{B_1i} + J^S) e_{B_1} \cdot e_i$ ($e_{B_1} \cdot e_i = 1$ for the ferromagnetically coupled atoms within the same chain and $e_{B_1} \cdot e_i = -1$ for the antiferromagnetically coupled atoms in neighboring chains) is positive, meaning that the magnetic equilibrium corresponds to the minimum of the total energy, and the magnetic moment at the site B_1 does not flip [19]. This results in the condition $|J^S| > J^D_{A_1B_2'}(\Delta_{\rm O}) + J^D_{B_1B_3} - J^D_{A_1B_1}$, which appears to be weaker than (9). Thus, the lower bound for $|J^S|$ is given by Eq. (9), and the upper bound is the same as in Eq. (7). The corresponding part of the phase diagram is shown in Fig. 2.

If the condition (9) is broken, the *CE* spin structure becomes unstable, and the CO state is melted [6]. Such a melting will be accompanied by the formation of the new FM bonds between zigzag chains. This will generally destroy the unique insulating feature of the quasi-1D zigzag chain, and the system will become metallic.

In summary, we have argued that the origin of the CO AFM phase in manganites lies in the unique electronic structure of the quasi-1D zigzag chain, which is the building block of the CO manganites one should look at.

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[21] Note that in the DE limit, the longer-range interactions between antiferromagnetically coupled atoms in neighboring zigzag chains are exactly cancelled with interactions in the FM chains arising from second order corrections to the minority-spin GF $\hat{\mathcal{G}}^{\downarrow}_{ji}(\varepsilon)$ of the form $(1/\Delta_{\rm ex}^2)\sum_{l\in 2, m\in 2} \hat{t}_{jl}\hat{G}_{lm}(\varepsilon)\hat{t}_{mi}$, where $i \in 1$ and $j \in 1$.