Orbital-order melting in rare-earth manganites: the role of super-exchange

Andreas Flesch,1 Guoren Zhang,1 Erik Koch,2 and Eva Pavarini1

1Institute for Advanced Simulation and JARA, Forschungszentrum Jülich, 52425 Jülich, Germany
2German Research School for Simulation Sciences, 52425 Jülich, Germany

We study the mechanism of orbital-order melting observed at temperature $T_{OO}$ in the series of rare-earth manganites. We find that many-body super-exchange yields a transition-temperature $T_{KK}$ that decreases with decreasing rare-earth radius, and increases with pressure, opposite to the experimental $T_{OO}$. We show that the tetragonal crystal-field splitting reduces $T_{KK}$ further increasing the discrepancies with experiments. This proves that super-exchange effects, although very efficient, in the light of the experimentally observed trends, play a minor role for the melting of orbital ordering in rare-earth manganites.

PACS numbers: 71.27.+a, 75.25.Dk, 71.30.+h, 71.28.+d, 71.10.Fd

The role of orbital degrees of freedom in the physics of LaMnO$_3$, and in particular the co-operative Jahn-Teller transition, has been debated since long. Ab-initio LDA+$U$ calculations show that Coulomb repulsion effects are key to understanding the orbitally-ordered antiferro-magnetic ground state. Super-exchange alone, however, is not sufficient to explain the persistence of Jahn-Teller distortions in the orbitally disordered phase, plays a major role in the orbital order-to-disorder transition (orbital order melting) observed at $T_{OO}$. Here we resolve this issue.

Remarkably, orbital-order melting has been observed in the full series of orthorhombic rare-earth (RE) manganites REMnO$_3$. These systems are perovskites with electronic configuration Mn 3d$^4$ ($t_2g$-$e_g$). In the co-operative Jahn-Teller phase ($T < T_{OO}$), the MnO$_6$ octahedra are tilted and rotated, and exhibit a sizable Jahn-Teller distortion with long and short MnO bonds antiferro-ordered in the $xy$ plane, and ferro-ordered along $z$ (Fig. 1). Neutron and X-ray diffraction data show that $T_{OO}$ increases from 750 K to $\sim 1500$ K with decreasing ionic radius IR (La $\rightarrow$ Dy) under increasing pressure eventually orbital order melts, while JT distortions still persist in nanoclusters.

The strength of super-exchange is directly linked to the amplitude of the hopping integrals, which depend on the cell volume and distortions. In the REMnO$_3$ series the volume decreases with ionic radius. Tilting and rotation, however, increase, because of the increasing mismatch between the Mn-O and RE-O bond-lengths. For LaMnO$_3$ a volume collapse at $T_{OO}$ has been reported. Under pressure, up to P=18 GPa the volume decreases by $\sim$ 10%, while tilting/rotation slightly decrease. A sizable volume reduction typically increases the Mn-O hopping integrals, while tilting and rotation tends to reduce them, reducing super-exchange effects. The scenario is further complicated by the local crystal-field, which can, depending on its size and symmetry, help or compete with super-exchange, and thus even reverse the trends.

In this Letter we clarify the role of super-exchange in orbital-melting. We show that, already in the absence of crystal-field splitting, only in LaMnO$_3$ $T_{KK} \sim T_{OO}$, while in all other systems $T_{KK}$ is 2-3 times smaller than $T_{OO}$: While $T_{OO}$ strongly increases with decreasing IR, $T_{KK}$ slightly decreases. Taking the tetragonal crystal-field splitting into account, these trends are enhanced even further. This proves that, although very large, in view of the reported experimental trends, super-exchange plays a minor role in the orbital-melting transition. In order to quantify the role of many-body super-exchange in determining $T_{OO}$, we perform ab-initio calculations based on the local density approximation (LDA) + dynamical mean-field theory (DMFT) method in the paramagnetic phase. The minimal model Hamiltonian to study super-exchange effects in manganites is the Hubbard model for the $e_g$ bands in the magnetic field

FIG. 1: (Color online) Orbital-order in TbMnO$_3$, as obtained by LDA+DMFT calculations. The pseudo-cubic axes pointing along Mn-Mn bonds are shown in the left corner.
first, we calculate the order parameter \( p \) as a function of temperature \( T \), in the second we determine the \( T = 0 \) total energy gain \( \Delta E(p) \) (Fig. 2) due to orbital order.

The order parameter for orbital-ordering is the orbital polarization \( p \equiv |n_1 - n_2| \), where [1] and [2] are the natural orbitals in \( e_g \)-space. To determine \( T_{\text{KK}} \) we perform LDA+DMFT calculations as a function of temperature for all materials in the series. They differ in (i) hopping integrals and (ii) crystal field, due to static distortions. In order to separate the effects of super-exchange from those of the crystal field, we perform LDA+DMFT calculations of the orbital polarization as a function of temperature for the real system (\( H^{\text{LDA}} \)), for ideal structures with the same hopping integrals but no crystal-field splitting (Fig. 3), and for ideal structures with only tetragonal splitting (Fig. 4).

In the second approach we calculate the energy gain due to orbital order from the difference in total energy between the orbitally polarized and the orbitally disordered states, in the absence of crystal fields (\( \varepsilon_T = \varepsilon_{JT} = 0 \)).

We perform LDA+DMFT calculations for decreasing temperature and calculate the total energy per formula unit and polarization \( p \), \( E_{\text{TOT}}(p) \). Next, we repeat the same procedure, but with the constraint \( p = 0 \) \((\Sigma_{1,1} = \Sigma_{2,2} \text{ and } \Sigma_{1,2} = 0)\).

The total energy is given by the following expression:

\[
E_{\text{TOT}}(p) = E_{\text{LDA}}^{\text{TOT}} + \langle H \rangle_p - E_{\text{eg}}^{\text{LDA}} - E_{\text{DC}},
\]

where \( E_{\text{LDA}}^{\text{TOT}} \) is the LDA total-energy, \( E_{\text{eg}}^{\text{LDA}} \) the thermal average of the \( 1 \) in the non-interacting \((U = 0, J = 0)\) case, \( \langle H \rangle_p \) the actual thermal average of \( 1 \) in DMFT for polarization \( p \), and \( E_{\text{DC}} \) the double counting correction.

Of all these terms only \( \langle H \rangle_p \) contributes to

\[
\Delta E(p) = E_{\text{TOT}}(p) - E_{\text{TOT}}(0) = \langle H \rangle_p - \langle H \rangle_{p=0}.
\]

\( \langle H \rangle_p \) can be split into a single-electron contribution (from the first three terms in \( 1 \)), which we calculate as sum on Matsubara frequencies, and a correlation contribution (from the last two terms in \( 1 \)), which we obtain from the double-occupancy matrix. Since \( -\Delta E_{\text{TOT}}(p) \sim 10 - 50 \) meV, error bars in particular the QMC statistical error on the double-occupancies matrix, have to be controlled to high accuracy [29].

The total-energy gain for \( \text{LaMnO}_3 \) is shown in Fig. 2. We obtain similar behavior for the other systems. In the zero-temperature limit, we extrapolate from \( \Delta E(p) \) the super-exchange energy gain \( \Delta E_{\text{KK}} = E_{\text{TOT}}(p = 1) - E_{\text{TOT}}(p = 0) \).

Remarkably, we find that the static mean-field [31] relation \( T_{\text{KK}} = |2 \Delta E_{\text{KK}}|/E_{\text{K}} \), which is valid for spin-1/2 Heisenberg-like model [1] with arbitrary coupling constants, gives transition temperatures close to those obtained from order-parameter calculations, the difference being a mere small shift. Our results are shown in Fig. 3. While \( T_{\text{KK}} \sim T_{\text{OO}} \) in \( \text{LaMnO}_3 \), in all other systems \( T_{\text{KK}} \) is a factor 2-3 smaller than the experimental estimate for \( T_{\text{OO}} \). Moreover, \( T_{\text{KK}} \) is maximum in...
LaMnO$_3$, and roughly decreases with IR from RE=La to Tb, then increases again. $T_{\text{KK}}$ also increases under pressure. These trends are opposite to those reported experimentally for the orbital melting temperature. They can be ascribed to the increasing distortions along the REMnO$_3$ series, and the decrease in volume and tilting/rotation with increasing pressure. Finally, for all systems super-exchange favors the occupation of the orbital (signs are given for the site displayed in Fig. 1) $|\theta\rangle=-\sin\frac{\theta}{2}|x^2-y^2\rangle+\cos\frac{\theta}{2}|z^2-1\rangle$, with $\theta=90^\circ$, while experimentally $\theta \sim 108^\circ$ in LaMnO$_3$ increasing with decreasing IR to 114$^\circ$ in TbMnO$_3$.

Due to the competition between the tetragonal crystal-field splitting $\varepsilon_T$ and super-exchange (which favors the occupation of different orbitals), $T_{\text{KK}}$ is reduced even further. We find that for finite $\varepsilon_T$ the system is orbitally ordered already at high temperature due to the crystal field, but the occupied orbital has $\theta = 180^\circ$. In Fig. 2 we show the results for $\varepsilon_T$ fixed at $\sim 130$ meV, sizable but smaller than for any of the considered systems (see Fig. 3). We find that at the reduced critical temperature $T_{\text{KK}}^{\varepsilon_T}$, super-exchange rotates the orbital towards $90^\circ$. The change in $T_{\text{KK}}$ is small for LaMnO$_3$, but $T_{\text{KK}}$ is reduced to 400 K for NdMnO$_3$, and even more for DyMnO$_3$ and TbMnO$_3$. Furthermore, in the zero-temperature limit, the smaller $T_{\text{KK}}^{\varepsilon_T}$, the closer is $\theta$ to $180^\circ$. Thus a fixed $\varepsilon_T \sim 130$ meV enhances the trend found for $\varepsilon_T = 0$: $T_{\text{KK}}$ is larger in LaMnO$_3$, and decreases going to DyMnO$_3$. Still, even for LaMnO$_3$, $\theta$ is significantly larger than the experimental $108^\circ$. This means that a Jahn-Teller crystal-field splitting $\varepsilon_{JT}$ is necessary to explain the experimental $\theta$; Fig. 4 shows that such splitting has to increase for the series RE=La, Nd, Dy, Tb. Taking into account that tetragonal splitting actually increases with decreasing pressure, and substituting La with Nd, Tb, or Dy (Fig. 3), this trend is enhanced even more. For $\varepsilon_T$ corresponding to the real structures, down to 150 K we find no super-exchange transition for all systems but LaMnO$_3$. These results can be understood qualitatively in static mean-field theory. In this approach, super-exchange yields an effective Jahn-Teller splitting $\varepsilon_{KK} = \langle \tau_z \rangle \lambda_{KK}$, where $\lambda_{KK}$ is the molecular field parameter; the self-consistency condition for orbital order is $\langle \tau_z \rangle = \frac{1}{2} \sin \theta \tanh \left( \beta \sqrt{\varepsilon_T^2 + \varepsilon_{KK}^2} \right)$, with $\sin \theta = \varepsilon_{KK}/\sqrt{\varepsilon_T^2 + \varepsilon_{KK}^2}$. This equation has a non-trivial solution ($\theta \neq 180^\circ$) only if $\lambda_{KK}/2 > \varepsilon_T$. The critical temperature is $T_{\text{KK}}^{\varepsilon_{KK}}/T_{\text{DO}} = (\varepsilon_T/2k_BT_{\text{DO}}^{\varepsilon_{KK}})/\tanh^{-1}(\varepsilon_T/2k_BT_{\text{DO}}^{\varepsilon_{KK}})$, with $k_BT_{\text{DO}}^{\varepsilon_{KK}} = \lambda_{KK}/4$; it decreases with increasing $\varepsilon_T$, while $\theta \rightarrow 180^\circ$ for large enough $\varepsilon_T$ ($\varepsilon_T > \lambda_{KK}/2$) there is no super-exchange driven transition at all.

In conclusion, for the orbital-melting transition in rare-earth manganites REMnO$_3$, we find that many-body super-exchange yields a transition temperature $T_{\text{KK}}$ very close to $T_{\text{DO}}$ only in LaMnO$_3$, while in all other systems $T_{\text{KK}}$ is less than half $T_{\text{DO}}$. Moreover, we find that super-exchange yields $\theta \sim 90^\circ$ for the occupied orbital, while in the experimental structures $\theta \sim 108^\circ - 114^\circ$. We also find that a tetragonal splitting $\varepsilon_T$ reduces $T_{\text{KK}}$ even further. $\varepsilon_T$ increases substituting La with Nd, Tb or Dy and decreases under pressure. Finally, super-exchange effects become larger with increasing pressure, while experimentally orbital order eventually melts.

We thank I. Loa and K. Syassen for sharing unpublished data. Calculations were done on the Jülich Blue Gene/P. We acknowledge financial support from the
Deutsche Forschungsgemeinschaft through research unit FOR1346.

* Electronic address: e.pavarini@fz-juelich.de

[1] K.I. Kugel and D.I. Khomskii, Zh. Eksp. Teor. Fiz. 64, 1429 (1973) [Sov. Phys. JETP 37, 725 (1973)].
[2] J.B. Goodenough, Phys. Rev. 100, 564 (1955); J. Kanamori, J. Appl. Phys. Suppl. 31, 148 (1960).
[3] Y. Tokura and N. Nagaosa, Science 288, 462 (2000); S.-W. Cheong, Nature Materials 6, 927 (2007); E. Dagotto and Y. Tokura, MRS Bull. 33, 1037 (2008); M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[4] W.-G. Yin, D. Volja, and W. Ku, Phys. Rev. Lett. 96, 116405 (2006).
[5] D. Feinberg, P. Germain, M. Grilli, and G. Seibold, Phys. Rev. B 57, R5583 (1998); C. Lin and A. J. Millis, Phys. Rev. B, 78, 174419 (2008).
[6] E. Pavarini, E. Koch, A.I. Lichtenstein, Phys. Rev. Lett. 101, 266405 (2008); E. Pavarini and E. Koch, Phys. Rev. Lett. 104, 086402 (2010).
[7] M.C. Sánchez, G. Subías, J. García, and J. Blasco, Phys. Rev. Lett. 90, 045503 (2003); X. Qiu, Th. Proffen, J.F. Mitchell, and S.J.L. Billinge, *ibid.* 94, 177203 (2005); A. Sartbaeva et al., *ibid.* 99, 155503 (2007).
[8] A. Y. Ramos et al., Phys. Rev. B 75, 052103 (2007); M. Baldini et al., Phys. Rev. Lett. 106, 066402 (2011).
[9] J. Rodriguez-Carvajal et al., Phys. Rev. B 57, R3189 (1998); Y. Murakami et al., Phys. Rev. Lett. 81, 582 (1998).
[10] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B 68, 144406 (2003); J.-S. Zhou and J. B. Goodenough, Phys. Rev. Lett. 96, 247202 (2006).
[11] B. Dabrowski et al., J. Solid State Chem. 178, 629 (2005).
[12] G. Maris, V. Volotchaev, and T.T.M. Palstra, New. J. Phys. 6, 153 (2004).
[13] I. Loa et al., Phys. Rev. Lett. 87, 125501 (2001); I. Loa and K. Syassen, private communication.
[14] J. M. Chen et al., Phys. Rev. B 79, 165110 (2009).
[15] T. Maitra, P. Thalmeier, and T. Chatterji, Phys. Rev. B 69, 132417 (2004).
[16] E. Gorelov et al., Phys. Rev. Lett. 104, 226401 (2010).
[17] E. Pavarini et al., Phys. Rev. Lett. 92, 176403 (2004).
[18] V. Anisimov et al., J. Phys.: Condens. Matter 9, 7359 (1997); A. I. Lichtenstein and M. I. Katsnelson, Phys. Rev. B 57 6884 (1998).
[19] K.H. Ahn, A.J. Millis, Phys. Rev. B 61, 13545 (2000). In the high-spin regime the orbital superexchange coupling depends weakly on $u_{a-a}$ terms [8]; thus we neglect them.
[20] See E. Pavarini, A. Yamasaki, J. Nuss and O. K. Andersen, New J. Phys. 7, 188 (2005).
[21] T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).
[22] A. Yamasaki et al., Phys. Rev. Lett. 96, 166401 (2006).
[23] A. Georges, G. Kotliar, W. Krauth, M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
[24] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. 56, 2521 (1986).
[25] P. Blaha, K. Schwarz, G. Madsen, D. Varsinska and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlsruhe Schwarz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2.
[26] A. A. Mostofi et al., Comp. Phys. Comm. 178, 685 (2008); J. Kunes et al., *ibid.* 181, 1888 (2010).
[27] LaMnO$_3$: $\varepsilon_T \sim 350$ meV, $\varepsilon_J > 650$ meV, $\varepsilon_{J1}^{001}$, $\varepsilon_{J2}^{011}$, $\varepsilon_{J3}^{101}$ = 392 meV, TbMnO$_3$: $\varepsilon_T$ $\sim 580$ meV, $\varepsilon_J$ $\sim 1060$ meV, $\varepsilon_{J1}^{001}$, $\varepsilon_{J2}^{011}$, $\varepsilon_{J3}^{101}$ = 349 meV. See Fig. [5] for comparison with NMTO results.
[28] A. K. McMahan, K. Held, and R. T. Scalettar, Phys. Rev. B 67, 075108 (2003); B. Amadon, S. Biermann, A. Georges, and F. Aryasetiawan, Phys. Rev. Lett. 96, 066402 (2006); I. Leonov et al., Phys. Rev. Lett. 101, 096405 (2008).
[29] A simple estimate from the average correlation energy, $\frac{1}{2} U n_{e_0} (n_{e_0} - 1) - \frac{1}{2} \langle U (2n_{e_0} - 1) - \delta n_{e_0} - \Delta E(p) \rangle$, which for $\Delta E(p)$ $\sim 10$ meV, $n_{e_0} = 1$ and $U = 5$ eV, yields $\delta n_{e_0} \approx 4 \cdot 10^{-3}$.
[30] All results shown are for $U = 5$ eV and $J = 0.75$ eV. For $P = 9.87$ GPa, setting $\varepsilon_T = \varepsilon_J = 0$ we obtain however a metallic solution with $p = 0$. Since $T_KK$ decreases with $U$ roughly as $1/U$, as expected from super-exchange theory, to compare values for constant $U$, we then extrapolate the $U = 5$ eV value of $T_KK$ from the insulating state obtained for slightly larger $U (U = 5.5$ eV, $U = 6$ eV).
[31] W. Nolting and A. Ramakranth, Quantum theory of Magnetism, Springer (2009), p. 306.
[32] M.W. Kim et al., Phys. Rev. Lett. 96, 247205 (2006).
[33] The energy gain due to the pseudospin rotation is $2|\Delta E|/k_BT_{KK}^e = (1 - x^2)(\tanh^{-1} x)/x$, where $x = 2\varepsilon_T/k_BT_{KK}$. For $\theta = 130^\circ$ (as for LaMnO$_3$, Fig. [4]) we find $T_{KK}^e \sim 0.47T_{KK}$ and $2|\Delta E|/k_BT_{KK}^e \sim 0.15$. This ratio is in qualitative agreement with what we find with DMFT for LaMnO$_3$, $|\Delta E| \sim 10$ meV.
[34] J. A. Alonso et al., Inorg. Chem. 39, 917 (2000).
[35] T. Mori et al., Mat. Lett. 54, 238 (2002).
[36] K. Uusi-Esko et al., Mater. Chem. Phys. 112, 1029 (2008).