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# Scaling of the transition temperature of hole-doped cuprate superconductors with the charge-transfer energy

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**Abstract** – We use first-principles calculations to extract two essential microscopic parameters, the charge-transfer energy and the inter-cell oxygen-oxygen hopping, which correlate with the maximum superconducting transition temperature $T_{c,max}$ across the cuprates. We explore the superconducting state in the three-band model of the copper-oxygen planes using cluster Dynamical Mean-Field Theory. We find that the variation in the charge-transfer energy largely accounts for the empirical trend in $T_{c,max}$, resolving a long-standing contradiction with theoretical calculations.



**Introduction.** – Despite an immense body of theoretical and experimental work, we have limited microscopic insights of which materials-specific parameters govern the trends in the maximum transition temperature $T_{c,max}$ across the copper oxide superconductors. Structurally, all the cuprate families have in common $CuO_2$ planes which support superconductivity. They are described by the chemical formula $XS_{n-1}(CuO_2)_n$, where $n$ $CuO_2$ planes are interleaved with $n-1$ spacer layers $S$ to form a multi-layer. These multi-layers are then stacked along the $c$-axis, separated by a different spacer layer $X$. Empirically, it is known that $T_{c,max}$ is strongly materials-dependent, ranging from 40 K in $La_2CuO_4$ to 138 K in $HgBa_2Ca_2Cu_3O_8$. Additionally, $T_{c,max}$ can be tuned both as a function of doping and the number $n$ of $CuO_2$ planes.

Studies linking the known empirical trends to microscopics have generally established that the properties of the apical atoms (O, F or Cl, depending on the cuprate family) are the relevant materials-dependent parameters. However, conclusions vary regarding their effects on electronic properties, especially in multi-layer cuprates where not all $CuO_2$ have apical atoms. Early theoretical work by Ohta, *et al.*, found correlations between $T_c$ and the Madelung potential of the apical oxygen, arguing that the apical potential controls the stability of the Zhang-Rice singlets [1]. They conclude that $d^{\text{apical}}_{\text{Cu-O}}$, the distance between the Cu and apical O, is uncorrelated with superconductivity. In a more recent DFT study, Pavarini *et al.*, argue that $d^{\text{apical}}_{\text{Cu-O}}$ tunes between the single-layer cuprate families, affecting the electronic structure primarily via the one-electron part of the Hamiltonian [2]. Moving the apical oxygens away from the copper oxide plane allows stronger coupling of in-plane O $2p$ orbitals to the Cu $4s$, enhancing the strength of longer ranged hoppings. This effect is characterized by the increase of a range parameter $r \sim t'/t$, describing the relative strength of the next-nearest-neighbor hopping $t'$ to nearest-neighbor hopping $t$ in a one-band model. They find that materials with larger $r$ have larger $T_{c,max}$. Many-body corrections to $t'$ were included by Yin *et al.* [3].

The development of cluster Dynamical Mean-Field Theory (c-DMFT) combined with first-principles calculations [4,5] has advanced our qualitative and quantitative understanding of the cuprates [6,7]. A satisfactory description of these materials at intermediate energy scales has been achieved, and the consensus is that the cuprates lie in the regime of intermediate correlation strength [8–10] near the Zaanen-Sawatzky-Allen (ZSA) boundary [11]. However, all numerical studies [12–14] contradict the empirical trend of $T_{c,max}$ with the range parameter $r$.

In this paper, we address the origin of the variation of the experimental $T_{c,max}$ across the cuprates using recent advances in electronic structure methods. We carry out first-principles calculations of the hole-doped cuprates, extract chemical parameters by downfolding to the 3-band

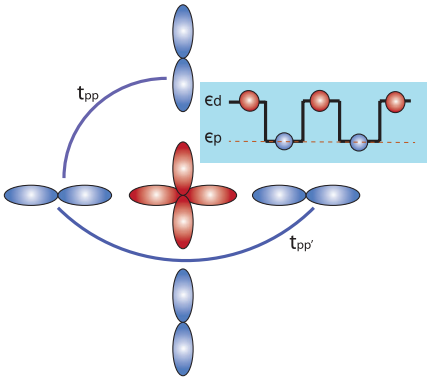


Fig. 1: Parameters of the three-band $p$-$d$ model for the $CuO_2$ planes in the cuprate superconductors. We show the two shortest-ranged oxygen-oxygen hoppings $t_{pp}$ and $t_{pp'}$, and the on-site energies $\epsilon_d$ and $\epsilon_p$.

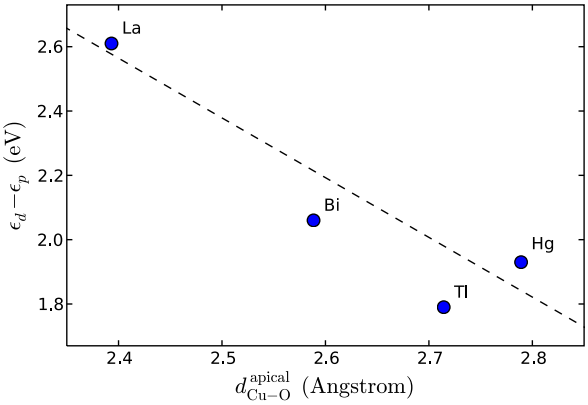


Fig. 2: In single-layer cuprates, increasing the apical oxygen distance reduces the charge-transfer energy.

$p$-$d$ model, and correlate them against $T_{\text{c,max}}$. Using c-DMFT, we explore the superconducting state and identify which parameter is the key driver of transition temperatures, resolving the conflict between numerics and the empirical findings of ref. [2]. We conclude with suggestions for possible improvements in materials design to reach higher critical temperatures.

**Trends in chemical parameters.** – Effective low-energy Hamiltonians containing the minimal set of bands are important tools for understanding chemical trends. We use the Wien2K code [15] to perform Linearized Augmented Plane Wave (LAPW) calculations on all major copper oxide families, and then extract model Hamiltonian parameters by downfolding [16] to orbitals constructed in the manner described in ref. [17]. In this work, we choose to downfold to a 3-band Hamiltonian describing the in-plane Cu-3$d_{x^2-y^2}$ and O-2$p$ orbitals (fig. 1). We believe four parameters capture the essential physics: the charge-transfer energy $\epsilon_d - \epsilon_p$ between the Cu and O atoms, the direct Cu-O hopping $t_{pd}$ and the two shortest-ranged O-O hoppings $t_{pp}$, and $t_{pp'}$. The extracted values are tabulated in the supplementary material [18].

We find that only two parameters, $\epsilon_d - \epsilon_p$ and $t_{pp'}$, vary significantly across the cuprates. Although not crucial for our subsequent work, one would like to have a simple structural explanation for these trends. For the single-layer cuprates, the variation can be directly connected to $d^{\text{apical}}_{\text{Cu-O}}$ (also tabulated in the supplementary material [18]). As we bring the negatively-charged apical oxygen towards the CuO plane, the resulting electrostatic repulsion suppresses the hopping $t_{pp'}$, since $t_{pp'}$ describes transitions of electrons past the Cu site, and provides justification for fact that $t_{pp'}$ is smaller than $t_{pp}$ [12]. This mechanism for the dependence of hoppings on $d^{\text{apical}}_{\text{Cu-O}}$ has been pointed out in ref. [2] for one-band models. However, we show in fig. 2 that the electrostatic repulsion simultaneously increases $\epsilon_d - \epsilon_p$ by rendering it costly to place an electron on the Cu site. These simple structural trends are less clear for multi-layer cuprates, where additional variables such as the inter-layer distance introduce additional complexity.

Having identified the two relevant parameters, we plot $T_{\text{c,max}}$ against these quantities in fig. 3(a) and fig. 3(b) to identify possible correlations. Beginning with $La_2CuO_4$ (LSCO), the limiting case among the cuprates since it has the largest $\epsilon_d - \epsilon_p$ as well as the smallest $t_{pp'}$, the figures show that both i) decreasing $\epsilon_d - \epsilon_p$ and ii) increasing $t_{pp'}$ correlate with an enhanced $T_{\text{c,max}}$. To map our results to the one-band Hubbard model, we integrate out the oxygen orbitals to extract the range parameter $r \sim t'/t$ (shown in fig. 3(c)), and use the fact that the effective one-band correlation strength is controlled by $\epsilon_d - \epsilon_p$ in charge-transfer materials [19]. Our results show that both the *correlation strength* and *range parameter* vary significantly across the cuprates, in contrast with ref. [2] which focused only on the latter.

**Correlation *vs.* causation.** – In order to clarify how the identified microscopic parameters control $T_{\text{c,max}}$, we use c-DMFT in the cellular form [4,5] with a $2 \times 2$ cluster of impurities to solve the downfolded three-band model. The non-local self-energy in c-DMFT captures the short-ranged correlations which are crucial to describe $d$-wave superconductivity. Since the fermionic minus sign problem prevents impurity solvers based on quantum Monte Carlo from accessing the low-temperature superconducting regime, we use finite-temperature exact diagonalization (ED) at $T = 30\,\text{K}$ as the impurity solver [20]. In this work, we extend previous c-DMFT calculations of the one-band model [13,21] to the three-band model, with realistic parameters obtained from first-principles calculations. The refinement captures the admixture of the Cu and O character near the Fermi level via a bath representing both the Cu and O degrees of freedom in the DMFT self-consistency condition.

The three-band Hamiltonian we treat with c-DMFT is as follows:

$$H = \sum_{i\alpha j\beta\sigma} t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} + \sum_{i\alpha\sigma} \epsilon_{\alpha} n_{i\alpha\sigma} + U_{dd} \sum_{i\sigma} n_{id\uparrow} n_{id\downarrow}, \quad (1)$$

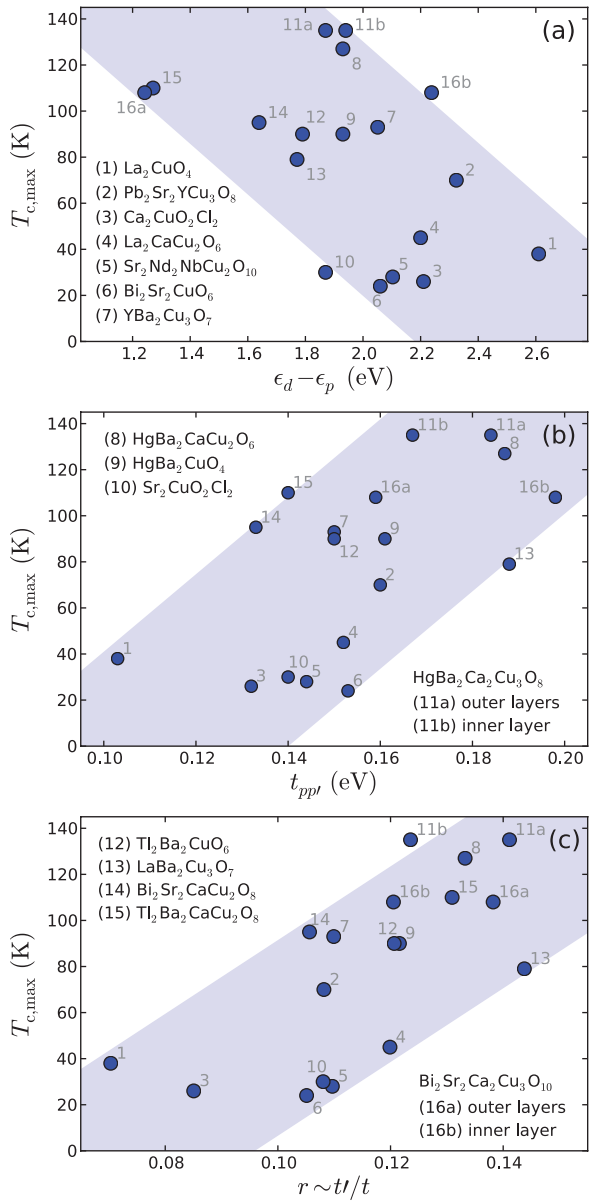


Fig. 3: Correlations of $T_{\mathrm{c,max}}$ in the copper oxides with the microscopic parameters of the three-band model Hamiltonian with (a) the charge-transfer energy $\epsilon_d - \epsilon_p$ (b) the next-nearest neighbor oxygen-oxygen hopping $t_{pp'}$ (c) the effective one-band range parameter $r \sim t'/t$. The trend of the dependence of the one-band range parameter agrees with ref. [2].

where $i, j$ run over the in-plane $CuO_2$ unit cells, $\alpha, \beta$ label the orbitals $p_x$, $p_y$ and $d_{x^2-y^2}$, and $\sigma$ is the electron spin. The hoppings $t_{ij}^{\alpha\beta}$ and onsite energies $\epsilon_\alpha$ are those sketched in fig. 1, except for the $d$-orbital onsite energy, where we subtract out a doping- and material-independent double-counting correction $E_{\mathrm{dc}}$ to account for correlations included in both LDA and DMFT. The atomic double-counting [22], which is very successful for all-electron DFT+DMFT [17], cannot be used because the Wannier functions of the three-band model significantly depart from the atomic wave functions. To determine $E_{\mathrm{dc}}$ for

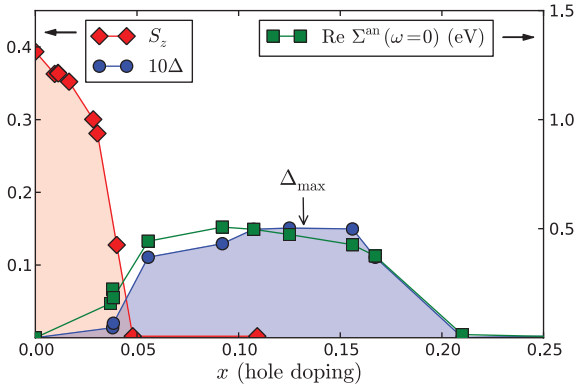


Fig. 4: Calculated doping dependence for LSCO of the staggered magnetization $S^z = \frac{1}{2}(n_\uparrow - n_\downarrow)$ and static $d$-wave superconducting order parameter $\Delta \sim \langle cc \rangle_{\tau=0}$. We plot $10\Delta$ to fit it on the same scale as $S^z$. Optimal superconducting strength $\Delta_{\mathrm{max}}$ is obtained for doping $x_{opt} \approx 0.13$. The real part of the anomalous self-energy $\mathrm{Re}\,\Sigma^{an}(\omega = 0)$ follows qualitatively the order parameter $\Delta$. The calculations were performed at $T = 30\,\mathrm{K}$ with c-DMFT and an ED impurity solver, using an 8-site discretization of the bath.

the Wannier representation, we match the low-energy Matsubara Green's function of the three-band model to the corresponding quantity in the *ab initio* all-electron calculation (see supplementary material [18]). A good match was attained for $E_{\mathrm{dc}} = 3.12\,\mathrm{eV}$ for an $d_{x^2-y^2}$ onsite Coulomb repulsion of $U_{dd} = 8\,\mathrm{eV}$.

To test our method, we use the extracted parameters for the canonical cuprate LSCO and explore the $T = 0$ phase diagram as a function of doping. Our results, shown in fig. 4, are qualitatively similar to experiment. The calculations stabilize antiferromagnetism for low dopings $x < 0.05$, which gives way to a dome of $d$-wave superconductivity. The static order parameter $\Delta = \langle\langle c_1 c_2 \rangle\rangle_{\tau=0}$, where 1 and 2 are nearest neighbor sites on the impurity plaquette, reaches a maximum $\Delta_{\mathrm{max}}$ near $x \sim 0.13$. We take the magnitude of $\Delta_{\mathrm{max}}$ as a proxy for the maximum superconducting temperature $T_{\mathrm{c,max}}$. The zero-frequency limit of the anomalous self-energy $\Sigma^{\mathrm{an}}$ is an additional indicator of superconductivity, which our results show qualitatively follows the magnitude of the order parameter.

We argue that although *two independent low-energy parameters* correlate with the experimental $T_{\mathrm{c,max}}$, it is the charge-transfer energy that controls the variation in $\Delta_{\mathrm{max}}$, and thus $T_{\mathrm{c,max}}$, across the cuprate families. To address this issue, we take the most correlated cuprate, LSCO, and compute $\Delta_{\mathrm{max}}$ as we either i) decrease $\epsilon_d - \epsilon_p$ or ii) increase $t_{pp'}$. Figure 5(a) shows that reducing the correlation strength for fixed $t_{pp'}$ enhances the order parameter $\Delta$, in agreement with the empirical trend in fig. 3(a). However, fig. 5(b) shows that increasing $t_{pp'}$ across the physical parameter regime hardly modifies $\Delta_{\mathrm{max}}$, in contrast with the empirical trend in fig. 3(b). Further increasing $t_{pp'}$ to larger, unphysical values strongly suppresses $T_{\mathrm{c,max}}$. Thus, our calculations support the hypothesis that a larger

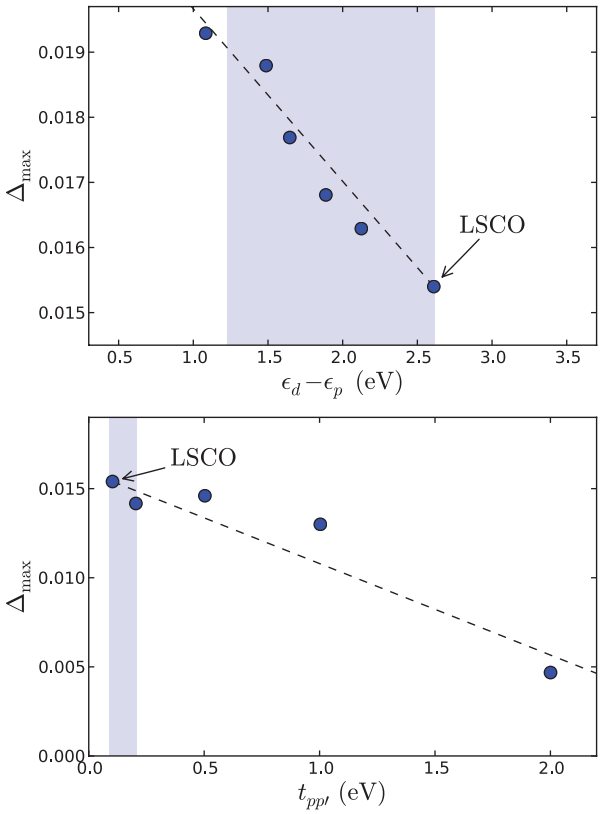


Fig. 5: Optimal superconducting order parameter $\Delta_{\max}$ of LSCO as we (a) decrease the charge-transfer energy $\epsilon_d - \epsilon_p$ and (b) increase oxygen-oxygen hopping $t_{pp'}$. Shaded are the physical ranges spanned by the cuprate families.

hopping range $r$ suppresses $T_{\mathrm{c,max}}$, in agreement with calculations on the one-band [13,14] and three-band [12] models.

The dependence of $T_{\mathrm{c,max}}$ on the two controlled parameters can be simply rationalized. For $\epsilon_d - \epsilon_p$, its large value in the strong correlation limit suppresses charge-fluctuations, rendering the residual superexchange interaction between the doped holes weak, resulting in low superconducting temperatures. As we decrease $\epsilon_d - \epsilon_p$, superconducting tendencies increase as we pass through the intermediate correlation regime, until we reach the weak correlation limit. Although the ground state of the 3-band model for large $U_{dd}$ and $\epsilon_d - \epsilon_p \sim 0$ has not been rigorously established, we expect the large kinetic energy to suppress the effective interactions and thus superconductivity. Thus, we believe intermediate correlation strengths, a regime intimately related to the charge-transfer metal-to-insulator transition, is a crucial ingredient for cuprate superconductivity. Turning to $t_{pp'}$, we find that increasing this hopping amplitude lowers the van Hove singularity at $(0, \pi)$ away from the Fermi level. The resulting decrease in density of states suppresses $T_{\mathrm{c}}$, an effect which simple methods capture [23]. We note, however, that calculations based on projected BCS states find the opposite trend [24], which warrants further examination.

**Conclusions.** – We have used electronic structure methods to identify the dependence of $T_{\mathrm{c,max}}$ on two fundamental parameters: the charge-transfer energy $\epsilon_d - \epsilon_p$ and inter-cell oxygen-oxygen hopping $t_{pp'}$. We find that the position of the apical oxygen tunes both parameters, but the strength of superconductivity, $\Delta_{\max}$, is mainly sensitive to $\epsilon_d - \epsilon_p$. We expect future refinements to explain the remaining variability in $T_{\mathrm{c,max}}$. Our work provides a natural interpretation of experiments where epitaxial compression in LSCO resulted in an enhancement of $T_{\mathrm{c}}$ [25]. Epitaxy increases $d^{\mathrm{apical}}_{\mathrm{Cu\text{-}O}}$ and thus reduces $\epsilon_d - \epsilon_p$. Furthermore, our result provides microscopic insight into the multi-layer cuprates, such as Bi-2223: in addition to layer-dependent doping [26], the smaller value of the charge-transfer energy in the outer layers may explain the enhancement of superconductivity in the outer layers. It has been suggested theoretically and demonstrated experimentally [27] that proximity to a metallic layer reduces the charge-transfer energy. Using this principle in heterostructure design should result in even higher transition temperatures.

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REFERENCES

[1] Ohta Y., Tohyama T. and Maekawa S., *Phys. Rev. B*, **43** (1991) 2968.
[2] Pavarini E., Dasgupta I., Saha-Dasgupta T., Jepsen O. and Andersen O. K., *Phys. Rev. Lett.*, **87** (2001) 047003.
[3] Yin W.-G. and Ku W., *Phys. Rev. B*, **79** (2009) 214512.
[4] Kotliar G., Savrasov S. Y., Haule K., Oudovenko V. S., Parcollet O. and Marianetti C. A., *Rev. Mod. Phys.*, **78** (2006) 865.
[5] Maier T., Jarrell M., Pruschke T. and Hettler M. H., *Rev. Mod. Phys.*, **77** (2005) 1027.
[6] Gull E., Parcollet O., Werner P. and Millis A. J., *Phys. Rev. B*, **80** (2009) 245102.
[7] Haule K. and Kotliar G., *Phys. Rev. B*, **76** (2007) 104509.
[8] Comanac A., de' Medici L., Capone M. and Millis A. J., *Nat. Phys.*, **4** (2008) 287.
[9] Weber C., Haule K. and Kotliar G., *Nat. Phys.*, **6** (2010) 574.
[10] Wang X., Gull E., de' Medici L., Capone M. and Millis A. J., *Phys. Rev. B*, **80** (2009) 045101.
[11] Zaanen J., Sawatzky G. A. and Allen J. W., *Phys. Rev. Lett.*, **55** (1985) 418.
[12] Kent P. R. C., Saha-Dasgupta T., Jepsen O., Andersen O. K., Macridin A., Maier T. A., Jarrell M. and Schulthess T. C., *Phys. Rev. B*, **78** (2008) 035132.

[13] Kancharla S. S., Kyung B., Sénéchal D., Civelli M., Capone M., Kotliar G. and Tremblay A.-M. S., *Phys. Rev. B*, **77** (2008) 184516.
[14] Maier T., Jarrell M., Pruschke T. and Keller J., *Phys. Rev. Lett.*, **85** (2000) 1524.
[15] Blaha P., Schwarz K., Madsen G. K. H., Kvasnicka D. and Luitz J., *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Technische Universität Wien, Austria) 2001.
[16] Souza I., Marzari N. and Vanderbilt D., *Phys. Rev. B*, **65** (2001) 035109.
[17] Haule K., Yee C.-H. and Kim K., *Phys. Rev. B*, **81** (2010) 195107.
[18] Weber C., Yee C.-H., Haule K. and Kotliar G., arXiv:1108.3028 (2011).
[19] Kotliar G., *Int. J. Mod. Phys. B*, **5** (1991) 341.
[20] Caffarel M. and Krauth W., *Phys. Rev. Lett.*, **72** (1994) 1545.
[21] Civelli M., *Phys. Rev. B*, **79** (2009) 195113.
[22] Anisimov V. I., Poteryaev A. I., Korotin M. A., Anokhin A. O. and Kotliar G., *J. Phys.: Condens. Matter*, **9** (1997) 7359, http://stacks.iop.org/0953-8984/9/i=35/a=010.
[23] Kotliar G. and Liu J., *Phys. Rev. B*, **38** (1988) 5142.
[24] Pathak S., Shenoy V. B., Randeria M. and Trivedi N., *Phys. Rev. Lett.*, **102** (2009) 027002, http://link.aps.org/doi/10.1103/PhysRevLett.102.027002.
[25] Locquet J.-P., Perret J., Fompeyrine J., Mchler E., Seo J. W. and Tendeloo G. V., *Nature*, **394** (1998) 453.
[26] Trokiner A., Le Noc L., Schneck J., Pougnet A. M., Mellet R., Primot J., Savary H., Gao Y. M. and Aubry S., *Phys. Rev. B*, **44** (1991) 2426.
[27] Altieri S., Tjeng L. H., Voogt F. C., Hibma T. and Sawatzky G. A., *Phys. Rev. B*, **59** (1999) R2517.