

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

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2012 EPL 100 37001

(<http://iopscience.iop.org/0295-5075/100/3/37001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 98.221.86.176

This content was downloaded on 14/10/2013 at 01:26

Please note that [terms and conditions apply](#).

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

C. WEBER¹, C. YEE², K. HAULE² and G. KOTLIAR²

¹ *T.C.M. Group - University of Cambridge, Cavendish Laboratory - J.J. Thomson Ave., Cambridge CB3 0HE, UK, EU*

² *Department of Physics and Astronomy, Rutgers University - Piscataway, NJ 08854-8019, USA*

received on 22 October 2012; accepted by S. Savrasov on 24 October 2012

published online 6 November 2012

PACS 74.72.Gh – Cuprate superconductors: Hole-doped

PACS 74.20.Pq – Electronic structure calculations

PACS 74.62.-c – Transition temperature variations, phase diagrams

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.



Copyright © EPLA, 2012

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 $XS_{n-1}(\text{CuO}_2)_n$, 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 $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$. 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 $d_{\text{Cu-O}}^{\text{apical}}$, the distance between the Cu and apical O, is uncorrelated with superconductivity. In a more recent DFT study, Pavarini *et al.*,

argue that $d_{\text{Cu-O}}^{\text{apical}}$ 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

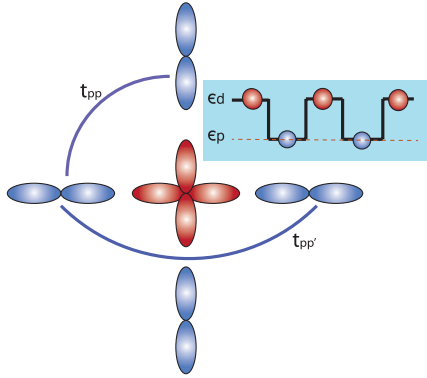


Fig. 1: Parameters of the three-band p - d model for the CuO_2 planes in the cuprate superconductors. We show the two shortest-ranged oxygen-oxygen hoppings t_{pp} and $t_{pp'}$, and the on-site energies ϵ_d and ϵ_p .

p - d model, and correlate them against $T_{c,\text{max}}$. 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 $\text{Cu-}3d_{x^2-y^2}$ and $\text{O-}2p$ 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 $d_{\text{Cu-O}}^{\text{apical}}$ (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 $d_{\text{Cu-O}}^{\text{apical}}$ 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

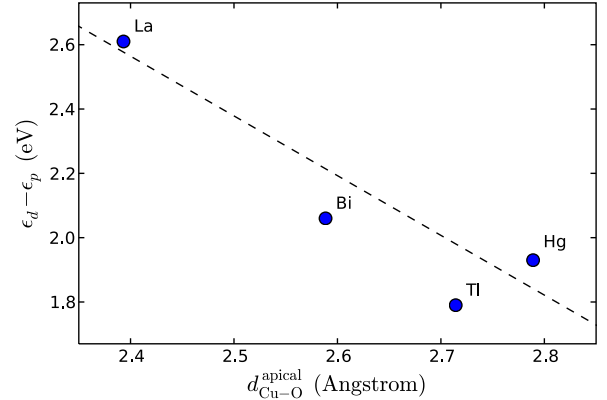


Fig. 2: In single-layer cuprates, increasing the apical oxygen distance reduces the charge-transfer energy.

multi-layer cuprates, where additional variables such as the inter-layer distance introduce additional complexity.

Having identified the two relevant parameters, we plot $T_{c,\text{max}}$ 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 $T_{c,\text{max}}$. 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 $T_{c,\text{max}}$, we use c-DMFT in the cellular form [4,5] with a 2×2 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 $T = 30$ 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:

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

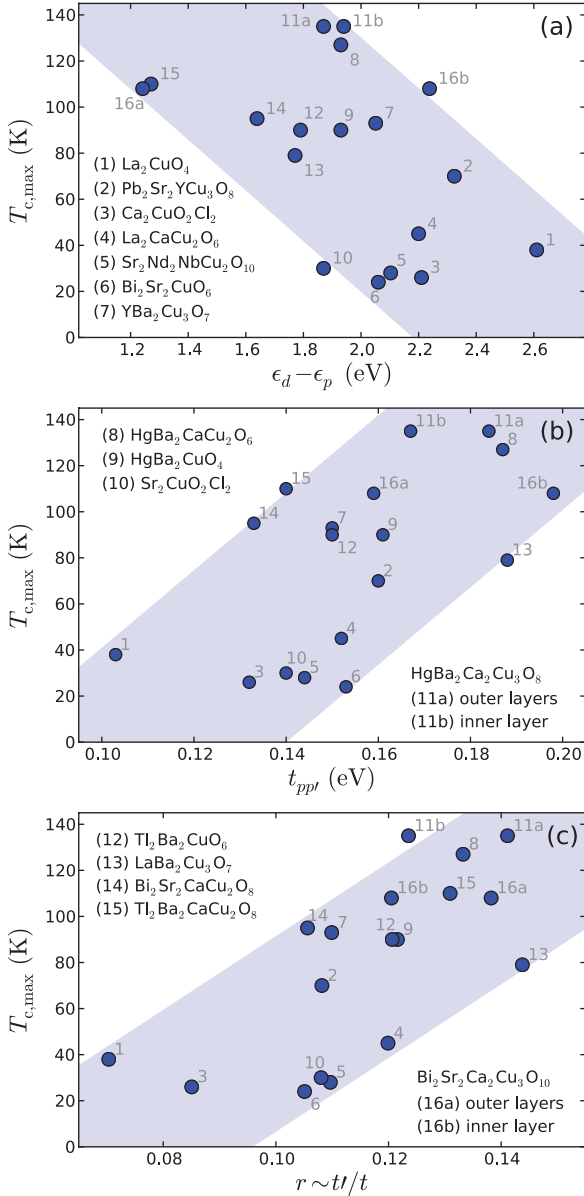


Fig. 3: Correlations of $T_{c,max}$ in the copper oxides with the microscopic parameters of the three-band model Hamiltonian with (a) the charge-transfer energy $\epsilon_d - \epsilon_p$ (b) the next-nearest neighbor oxygen-oxygen hopping $t_{pp'}$ (c) the effective one-band range parameter $r \sim t'/t$. 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, α, β label the orbitals p_x, p_y and $d_{x^2-y^2}$, and σ is the electron spin. The hoppings $t_{ij}^{\alpha\beta}$ and onsite energies ϵ_α 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_{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_{dc} for

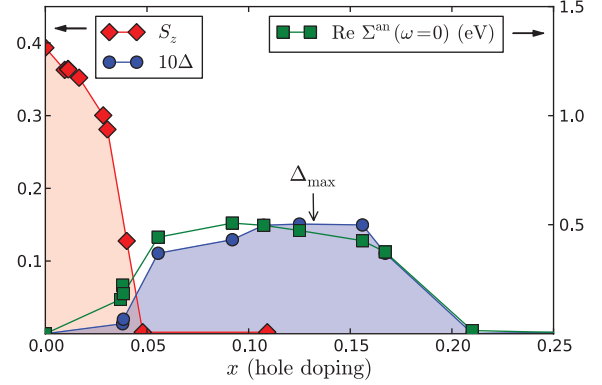


Fig. 4: Calculated doping dependence for LSCO of the staggered magnetization $S^z = \frac{1}{2}(n_\uparrow - n_\downarrow)$ and static d -wave superconducting order parameter $\Delta \sim \langle cc \rangle_{\tau=0}$. We plot 10Δ to fit it on the same scale as S^z . Optimal superconducting strength Δ_{max} is obtained for doping $x_{opt} \approx 0.13$. The real part of the anomalous self-energy $\text{Re } \Sigma^{an}(\omega=0)$ follows qualitatively the order parameter Δ . The calculations were performed at $T = 30$ 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 $E_{dc} = 3.12$ eV for an $d_{x^2-y^2}$ onsite Coulomb repulsion of $U_{dd} = 8$ 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 Δ_{max} near $x \sim 0.13$. We take the magnitude of Δ_{max} as a proxy for the maximum superconducting temperature $T_{c,max}$. The zero-frequency limit of the anomalous self-energy Σ^{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 $T_{c,max}$, it is the charge-transfer energy that controls the variation in Δ_{max} , and thus $T_{c,max}$, across the cuprate families. To address this issue, we take the most correlated cuprate, LSCO, and compute Δ_{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 Δ , 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 Δ_{max} , in contrast with the empirical trend in fig. 3(b). Further increasing $t_{pp'}$ to larger, unphysical values strongly suppresses $T_{c,max}$. Thus, our calculations support the hypothesis that a larger

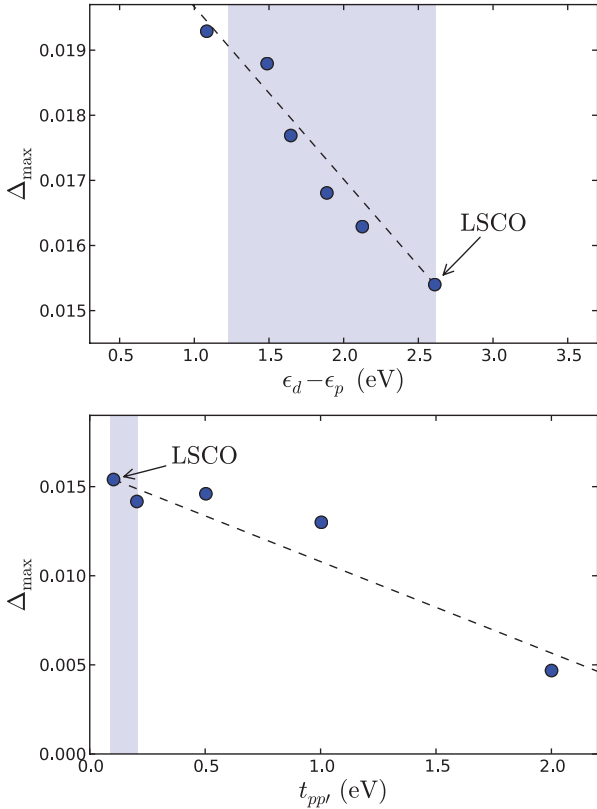


Fig. 5: Optimal superconducting order parameter Δ_{\max} of LSCO as we (a) decrease the charge-transfer energy $\epsilon_d - \epsilon_p$ and (b) increase oxygen-oxygen hopping $t_{pp'}$. Shaded are the physical ranges spanned by the cuprate families.

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

The dependence of $T_{c,\max}$ 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_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 $T_{c,\max}$ 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, Δ_{\max} , is mainly sensitive to $\epsilon_d - \epsilon_p$. We expect future refinements to explain the remaining variability in $T_{c,\max}$. Our work provides a natural interpretation of experiments where epitaxial compression in LSCO resulted in an enhancement of T_c [25]. Epitaxy increases $d_{\text{Cu-O}}^{\text{apical}}$ 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.

We thank A.-M. TREMBLAY and A. MILLIS for enlightening discussions. KH and CY were supported by NSF DMR-0746395, GK was supported by NSF DMR-0906943, CW was supported by Swiss National Foundation for Science.

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] ZAAENEN 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., RANDEIRA 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., VOGGT F. C., HIBMA T. and SAWATZKY G. A., *Phys. Rev. B*, **59** (1999) R2517.