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Spectral properties of the Mott Hubbard insulator $(Cr_{0.011}V_{0.989})_2O_3$ calculated by LDA+DMFT

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Abstract. Significant progress in the theoretical description of Mott-Hubbard metal-to-insulator transitions has been made in the last years, especially thanks to the LDA+DMFT approach (local density approximation + dynamical mean field theory). Obviously the main attention has been focused on the transition itself, as, for example, in the textbook case of the Cr-doped V_2O_3. As we discuss here, however, also the study of the insulating phase, characterized by the opening of a visible Mott-Hubbard gap in the spectral functions is far from being trivial: Strong-correlation effects make this phase strongly sensitive to small changes of external parameters, much more than one would expect for an insulator. In this situation, requiring a full consistency of the theoretical calculations with data from different spectroscopies may provide the most precise estimate for the local Coulomb interaction U in the LDA+DMFT approach.

1. Introduction

Much effort has been devoted in the past to the theoretical description of the Mott-Hubbard metal-to-insulator transition. In this respect, the most impressive results have been obtained so far by merging ab-initio density functional theory in the local density approximation (LDA) [1] with dynamical mean field theory [2] (DMFT). Within this LDA+DMFT [3] approach, for example, profound insight on the doping driven Mott transition in V_2O_3 has been gained [4, 5, 6, 7].

The LDA+DMFT method indeed allows us to include the effects of a local Coulomb electron-electron interaction (U), as well as the Hund exchange term J, starting from a realistic ab-initio LDA Hamiltonian for a given compound. The choice of the (material dependent) values U and J is of course a delicate step in this procedure. Usually, a reasonable estimate of these parameters can be obtained from the so-called "constrained LDA" method [8, 9, 10], where the extra-energy for adding an electron on a specific set of orbitals is computed. Such constrained LDA estimates are still affected by a relatively large uncertainty. However, the estimated U and the J values can account for the occurrence of the Mott-Hubbard transition in the material under consideration, the uncertainty in these values translating mainly into an uncertainty of the exact doping and pressure level of the transition. In this respect, even the earliest LDA+DMFT [4] studies on V_2O_3 were not only able to capture the main features of the photoemission spectroscopy across

the transition line of this material, but they also predicted the correct results of following higher resolution experiments [11].

As we discuss in this paper, however, a more precise choice of U and J, in the context of a complete treatment of the hybridization terms (due to hopping processes between different orbitals) in the LDA+DMFT Hamiltonian, can be a crucial factor for describing consistently the properties of the Mott insulating phase. Focusing on the textbook case of V_2O_3, we will show how strong the choice of the value of U affects the spectral gap and the occupation numbers for the different orbitals (i.e., quantities which can be directly compared to the experiments).

2. LDA+DMFT calculation for the insulating V_2O_3

We consider here the case of the 1.1% Cr-doped V_2O_3 in the insulating phase, whose lattice structure parameter have been taken from Ref. [12]. Starting point for our LDA+DMFT calculations is the Nth-order Muffin Tin Orbital (NMTO) downfolded Hamiltonian for the three t_{2g} Wannier functions (further splitted in two e_g^π and one a_{1g} orbital due to trigonal distortion) [5] of the vanadium atoms. Since the hybridization terms between the different t_{2g} orbitals play an important role in the physics of the Mott Hubbard transition [7], they have been fully taken into account when performing our LDA+DMFT calculations.

The interacting part of our LDA+DMFT Hamiltonian reads

$$H_{int} = U \sum_{i,m} n_{im,\uparrow} n_{im,\downarrow} + \frac{1}{2} \sum_{i,m \neq m',\sigma,\sigma'} (U - 2J - J\delta_{\sigma\sigma'})\, n_{im,\sigma} n_{im',\sigma'}$$

where the density operators $n_{im,\sigma} = c^\dagger_{im,\sigma} c_{im,\sigma}$ can be written through the creation/annihilation operators for one electron with spin σ on site i and orbital m, respectively.

As we are interested in analyzing specifically the role of the electron-electron interaction parameters, we have performed several different LDA+DMFT calculations for different value of the local Coulomb repulsion U. Following Ref. [7] we have assumed $J = 0.7$eV for the Hund's exchange energy and 4.2eV as a starting value for the energy U . The impurity model associated with our DMFT Hamiltonian has been solved by means of a Hirsch-Fye quantum Monte Carlo [13] algorithm (with Ulmke smoothing[14]) at a temperature of $\beta = 1/T = 20$ eV$^{-1} \simeq 590$K.

3. LDA+DMFT results

The main results of our LDA+DMFT calculation are reported in Fig. 1, where the evolution of the $k-$integrated spectral function $A(\omega)$ of the t_{2g} orbitals is reported as a function of the local Coulomb interaction. As it is quite evident from the first and the second panel of the Figure, a value of U of at least 4.0eV is needed to observe a clear depletion of the spectral function at the Fermi level, i.e. to describe the insulating side of the Mott Hubbard transition in V_2O_3.

It is remarkable, however, that for $U \geq 4.0$eV (i.e., for insulating solutions) a strong $U-$dependence of the low energy part of the spectra is also observed. In particular, the size of the spectral gap Δ is strongly dependent on small changes of U. A rough visual estimate gives values ranging from $\Delta \leq 0.5$ for $U = 4.0$ and $\Delta \sim 1.5$ eV for 4.2 eV, respectively. Hence a successful interpretation of spectroscopy experiments in the insulating phase will crucially depend on the value of U, whereas a description of the metal-to-insulator transition can be obtained without a precise estimate of the local Coulomb interaction.

Not surprisingly at this point, our LDA+DMFT calculation shows that also frequency-integrated properties, such as the occupation of the e_g^π and a_{1g} orbitals, depend crucially on small changes of the Coulomb interaction in the range we have considered. Note that this quantity is experimentally accessible through, e.g., X-ray absorption spectroscopy for the L-edge of the vanadium atom [16] and, as it has been extensively discussed [4, 16, 7], its value

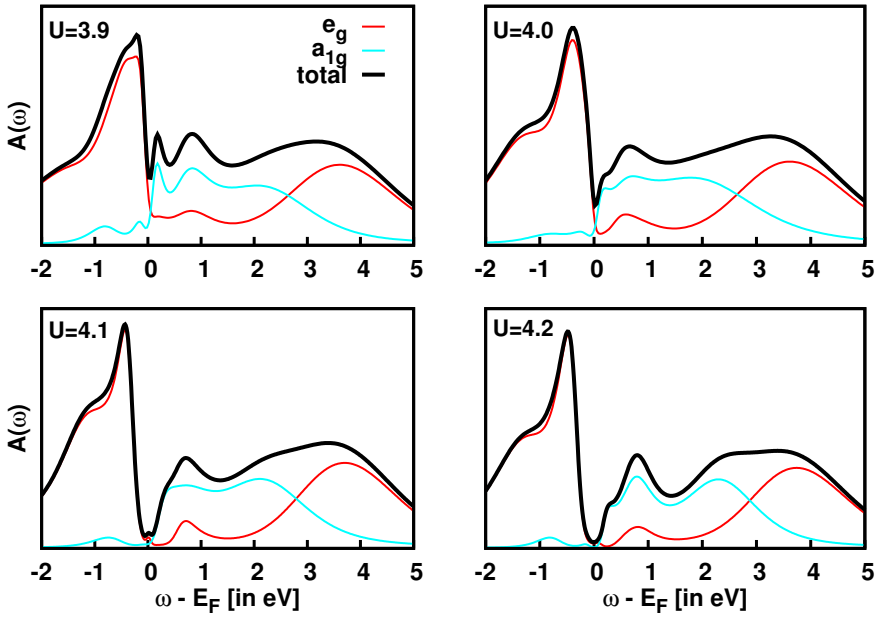

Figure 1. LDA+DMFT $k-$integrated spectral function projected onto the t_{2g} orbitals of 1.1% Cr-doped V_2O_3 (for the lattice structure correspondent to the insulating phase), and its partial contributions from e_g^π and a_{1g} orbitals for four different values of the Coulomb interaction U = 3.9, 4.0, 4.1 and 4.2eV. Note that a better statistic has been used for the Maximum Entropy[15] analytic continutation in the $U = 4.1$ and 4.2eV cases.

is probably the key to understand how the metal-to-insulator transition actually takes place in V_2O_3.

After a proper inclusion of the hybridization effects, our LDA+DMFT calculation gives a ratio for occupations e_g^π to a_{1g} orbitals of 4.3 and 4.9 for $U = 4.0$ and 4.2 eV, respectively, in the insulating phase of 1.1% Cr-doped V_2O_3. A comparison with the experimental estimate (4.0) by Park et al. [16] would suggest then to assume for the LDA+DMFT calculation a value closer to $U = 4.0$eV, i.e. slightly smaller than all the values considered for LDA+DMFT calculations for V_2O_3 so far.

It is clear, however, that the success of such a precise quantitative description of the LDA+DMFT relies on the possibility of using the same value of U to interpret consistently all the spectroscopic experiments: The same value of U should account for the estimated orbital occupation *and* for the size of the spectral gap. In this regard, new optical conductivity measurements in the insulating phase to be compared to correspondent LDA+DMFT calculations as done in Ref. [17, 18] for the metallic case would be strongly desirable. Optical measurements represent in fact one of the most reliable tools to estimate the absolute value of the spectral gap without running into the delicate problem of fixing the exact value of the chemical potential through an electrically coupled reference system.

4. Conclusions

In this paper, we have demonstrated that the theoretical prediction for the physical properties of a Mott-insulator, as the textbook example of Cr-doped V_2O_3 can be strongly affected by small changes of the parameter which defines the electron-electron interaction in the

theoretical(LDA+DMFT) calculations. While an important role of the precise value of the Coulomb interaction U is more naturally expected in the strongly renormalized metallic side of the Mott transition (it has even been recently proposed to exploit this situation for engineering the properties of strongly correlated heterostructures [19]), this was less obvious for the insulating phase. Turning to the comparison with the experiments, the results of X-ray absorption spectroscopy would suggest to assume a value of U slightly smaller than considered so far in the literature. On the other hand, our present analysis leaves still open the question whether and to what extent a full quantitative LDA+DMFT analysis can consistently describe all the spectroscopic experiments in the insulating phase. As we mentioned before, a close comparison of optical spectroscopy data with LDA+DMFT calculation should eventually help to clarify this point.

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References

[1] R.O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
[2] W. Metzner and D. Vollhardt, *Phys. Rev. Lett.* **62**, 324 (1989); A. Georges and G. Kotliar, *Phys. Rev. B* **45** 6479 (1992); A. Georges, G. Kotliar, W. Krauth, and M. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996); G. Kotliar and D. Vollhardt, *Physics Today* **57**, 53 (2004).
[3] V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin and G. Kotliar, *J. Phys. Cond. Matter* **9** 7359 (1997); A. I. Lichtenstein and M. I. Katsnelson, *Phys. Rev. B* **57** 6884 (1998); G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet and C. A. Marianetti, Rev. Mod. Phys. **78** 865 (2006); K. Held, *Advances in Physics*, **56**, 829 (2007).
[4] K. Held, G. Keller, V. Eyert, D. Vollhardt, and V. I. Anisimov, *Phys. Rev. Lett.* **86**, 5345 (2001); G. Keller, K. Held, V. Eyert, D. Vollhardt, and V. I. Anisimov, *Phys. Rev. B* 70, 205116 (2004).
[5] "Electronic structure of V_2O_3: Wannier orbitals from LDA-*N*MTO calculations", T. Saha-Dasgupta, O.K. Andersen, J. Nuss, A.I. Poteryaev, A. Georges, and A.I. Lichtenstein, arXiv:0907.2841.
[6] M. S. Laad, L. Craco and E. Müller-Hartmann, *Phys. Rev. Lett.* **91** 156402 (2003); *Phys. Rev. B* **73** 045109 (2006).
[7] A. I. Poteryaev, J. M. Tomczak, S. Biermann, A. Georges, A. I. Lichtenstein, A. N. Rubtsov, T. Saha-Dasgupta, and O. K. Andersen, *Phys. Rev. B* **76**, 085127 (2007).
[8] P. H. Dederichs, S. Blügel, R. Zeller and H. Akai, *Phys. Rev. Lett.* **53** 2512 (1984).
[9] A. K. McMahan, R. M. Martin and S. Satpathy, *Phys. Rev. B* **38** 6650 (1988).
[10] O. Gunnarsson, O. K. Andersen, O. Jepsen and J. Zaanen, *Phys. Rev. B* **39** 1708 (1989).
[11] S.-K. Mo, J. D. Denlinger, H.-D. Kim, J.-H. Park, J. W. Allen, A. Sekiyama, A. Yamasaki, K. Kadono, S. Suga, Y. Saitoh, T. Muro, P. Metcalf, G. Keller, K. Held, V. Eyert, V. I. Anisimov and D. Vollhardt, *Phys. Rev. Lett.* **90** 186403 (2003).
[12] W. R. Robinson *Acta Cryst.* B**31**, 1153-1160 (1975).
[13] J. E. Hirsch and R. M. Fye, *Phys. Rev. Lett.* **56** 2521 (1986).
[14] M. Ulmke, Eur. Phys. J. B bf 1, 310 (1998).
[15] M. Jarrell, and J. E. Gubernatis, *Physics Reports* **269**, 133, (1996).
[16] J.-H. Park, L. H. Tjeng, A. Tanaka, J. W. Allen, C. T. Chen, P. Metcalf, J. M. Honig, F. M. F. de Groot, and G. A. Sawatzky, *Phys. Rev. B* **61**, 11506 (2000).
[17] L. Baldassarre, A. Perucchi, D. Nicoletti, A. Toschi, G. Sangiovanni, K. Held, M. Capone, M. Ortolani, L. Malavasi, M. Marsi, P. Metcalf, P. Postorino, and S. Lupi, *Phys. Rev. B* **77**, 113107 (2008).
[18] J. M. Tomczak and S. Biermann, *Journal of Physics- Cond. Matt.* **21**, 064209 (2009).
[19] P. Hansmann, Xiaoping Yang, A. Toschi, G. Khaliullin, O. K. Andersen, and K. Held, *Phys. Rev. Lett.* **103**, 016401 (2009).