14th International Conference on X-Ray Absorption Fine Structure (XAFS14) IOP Publishing
Journal of Physics: Conference Series **190** (2009) 012092 doi:10.1088/1742-6596/190/1/012092

Electronic correlations in V_2O_3 studied with K-edge X-ray absorption spectroscopy

F. Rodolakis[1,2], P. Hansmann[3,4], J.-P. Rueff[2,5], A. Toschi[3], M.W. Haverkort[4], G. Sangiovanni[3], K. Held[3], M. Sikora[6], A. Congeduti[2], J.-P. Itié[2], F. Baudelet[2], P. Metcalf[7] and M. Marsi[1]

[1] Laboratoire de Physique des Solides, CNRS-UMR 8502, Université Paris-Sud, F-91405 Orsay, France
[2] Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France
[3] Institut for Solid State Physics, Vienna University of Technology, 1040 Vienna, Austria
[4]Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
[5]Laboratoire de Chimie Physique–Matière et Rayonnement, CNRS-UMR 7614, Université Pierre et Marie Curie, F-75005 Paris, France
[6]ESRF, 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex, France
[7]Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

E-mail: `fanny.rodolakis@synchrotron-soleil.fr`, `hansmann@ifp.tuwien.ac.at`

Abstract. We show that K-edge X-ray absorption spectroscopy can be used as a sensitive probe of electron correlations in V_2O_3. This is possible thanks to a detailed study of the V K pre-edge region while changing the thermodynamic parameters of the system. LDA+DMFT provides an interpretation of the changes in the electronic structure, in particular in the upper Hubbard band, at the Mott transition. The possibility of modifying the Coulomb interaction and observing the metal-insulator transition by applying an external pressure is also demonstrated, which is of particular interest for the study of many strongly correlated materials.

1. Introduction

Understanding phase transitions induced by strong electron correlations represents one of the major challenges in condensed matter physics[1]. Phenomena presenting great interest both from point of view of basic science and of their potential technological applications, like metal-insulator transitions and high temperature superconductivity, are typical examples of effects determined by collective electronic excitations. Despite their importance and decades of intensive theoretical and experimental research, our understanding of these effects is nevertheless far from complete. On the theoretical side, the development of dynamical mean field theory (DMFT) [2] provided a powerful conceptual approach to interpret these phenomena, and a considerable effort is currently under way to apply it to real materials in combination with other numerical methods like Local Density Approximation (LDA). On the experimental side, one of the main challenges for the study of strongly correlated materials is the development of techniques giving access to the electronic structure of these system while tuning different parameters (temperature, doping, pressure, etc.) across their often complicated thermodynamic phase diagram[3].

In this work we present the results of a collaborative effort which establishes a bridge between these two directions of research in the physics of strongly correlated systems, and show that K-edge X-ray Absorption Spectroscopy (XAS) can be a very sensitive method to measure electron correlation effects. With respect to L-edge XAS, routinely used to study transition metal oxides, K-edge spectroscopy presents a less complicated multiplet structure in the spectra, thanks to the simple $1s$ symmetry of the core hole; furthermore, it makes it possible to perform measurements while applying an external pressure, since hard X-rays have a good transmission through diamond anvil cells: this is critically important for the study of strongly correlated materials, because it discloses the possibility of changing one more very important parameter - pressure - while exploring the phase diagram of the system.

As a showcase, we present the analysis of the V K-edge in $(V_{1-x}Cr_x)_2O_3$. In the phase diagram of this system (see inset in Fig. 1), an isostructural transition can be found between a paramagnetic insulating (PI) and a paramagnetic metallic (PM) phase [4, 5], which has been for a long time considered as a poster child of Mott transition, determined only by the balance between kinetic energy of the electrons (t) and their Coulomb interaction (U). Varying t with respect to U determines the transition between two phases that have the same corundum structure, but present a difference in conductivity of seven orders of magnitude. This PI/PM transition has been the subject of many theoretical [6, 7, 8, 9, 10, 11, 12, 13] and experimental [14, 15, 16, 17, 18, 19, 20] studies for decades: here we show that V K-edge XAS compared with LDA+DMFT calculations can shine new light on the interpretation of this long standing problem.

2. Experimental details

The results presented here were obtained on powders prepared from high quality $(V_{1-x}Cr_x)_2O_3$ ($x = 0.011$) crystals. The metal-insulator transition was obtained either changing the temperature, during an experimental run on the ID-26 beamline at the ESRF, or applying an external pressure, during the measurements performed at the ODE beamline at SOLEIL.

The XAS spectra on ID-26 were acquired in partial fluorescence yield (PFY) mode, to take advantage of the narrow photon bandwidth (160 meV) of the X-ray beam, dispersed with a cryogenically cooled Si(311) double-crystal monochromator. The PFY mode made it possible to obtain high energy resolution spectra, detecting the V-Kα ($2p \rightarrow 1s$) line while the incident beam was swept across the absorption edge. The V-Kα fluorescence line was measured with a IXS Rowland-circle spectrometer equipped with a Ge(331) spherically bent analyzer with a radius of 0.86 m.

The PFY mode was instead not applicable during the measurements under pressure, due to the strong absorption of the diamond anvil cells used to apply high pressure on the specimens; the experiments at ODE were thus performed in transmission mode, with a reduced energy resolution but allowing the simultaneous collection of a wide spectral range thanks to the dispersive optical setup of the beamline. Pressure was applied by means of composite anvils made of perforated diamond capped with a 500 μm thin diamond anvil, using silicon oil as transmitting medium. The applied pressure was measured using the standard ruby fluorescence technique.

3. Theoretical approach

The strong electronic correlation between the d-electrons of the V atoms, which - as it is widely known - is responsible for the occurrence of the Metal-Insulator Mott-Hubbard transition in V_2O_3, makes the Local Density Functional (LDA)[21] schemes inadequate for describing the physics of this compound in an energy window of some eVs around the Fermi level E_F. A theoretical calculation of the electronic structure of V_2O_3, i.e., of the spectral functions to be compared with the experiments, has hence no chance to be successful without a proper inclusion of the electron-electron interaction. At present one of the most powerful techniques to achieve

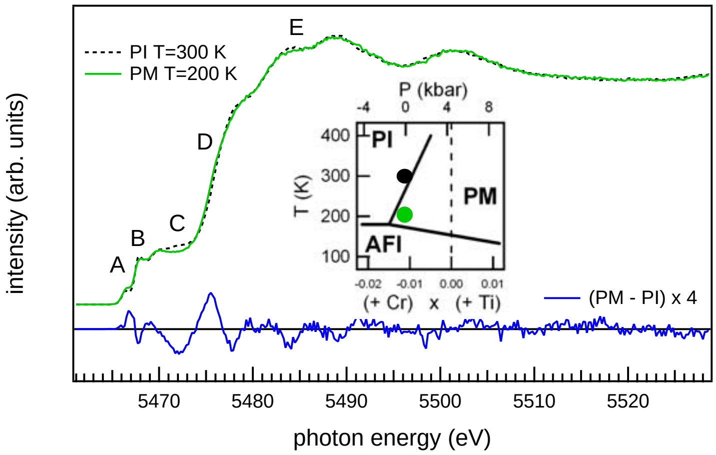

Figure 1. The PM-PI transition in $(V_{1-x}Cr_x)_2O_3$ ($x = 0.011$) as observed with V K edge XAS.

this goal is DMFT[2]. In DMFT, the original (and extremely complicated) interacting lattice problem is mapped onto a self-consistent impurity problem, where an exact treatment (e.g.. via Hirsh-Fye Quantum Monte Carlo) of the most important part of the Coulomb interaction, namely the local one (U), becomes possible.

In order to analyze spectral functions corresponding to processes involving the d-orbitals in V_2O_3, as it is the case for the photoemission spectra close to E_F or the V-$K-$pre-edge XAS spectra, one has to implement the LDA results for the corresponding orbitals with the DMFT algorithm, in the so-called LDA+DMFT scheme (LDA will be instead sufficient, far from E_F, in the region where processes involving $p-$orbitals are dominant). The LDA+DMFT scheme has been already proved to work extremely well to understand the photoemission spectra in this compound[7, 9, 10], and it will be applied here for analyzing the XAS spectra in the pre-edge region. In this regard, an important difference should be pointed out: in contrast to the case of the photoemission spectra, in the case of XAS excitonic effects due to the formation of the core-hole in the measuring process prevent the direct observation of what would correspond to the “coherent part” of the spectrum in photoemission. On the other hand, the “incoherent-part” of the spectrum (represented by the so-called “upper Hubbard band”, UHB) can be determined with an high degree of accuracy. This allows the evaluation of important parameters of the systems, e.g. the Hund coupling constant J, for which, so far, only very gross theoretical predictions were available.

4. Results and discussion

In Fig. 1 we present typical examples of V K-edge XAS spectra on $(V_{1-x}Cr_x)_2O_3$, in agreement with previous studies [22, 23, 24]: in particular, these spectra were taken on a ($x = 0.011$) powder at 300 K (PI phase) and 200 K (PM phase). The possibility of observing the small but clearly detectable difference between the two phases is at the basis of our efforts: since the PM and PI phases have the same crystal structure, the difference PM-PI plotted in Fig. 1 shows that our probe is sufficiently sensitive to detect differences in the electronic structure which are mainly due to the effects of electron correlations.

As one can see, the differences are more visible in certain regions of the spectrum, namely the pre-edge (peaks A, B and region C), on the onset (D) and when the plateau of the main edge (E) is reached; at energies higher than E, the two spectra are virtually indistinguishible.

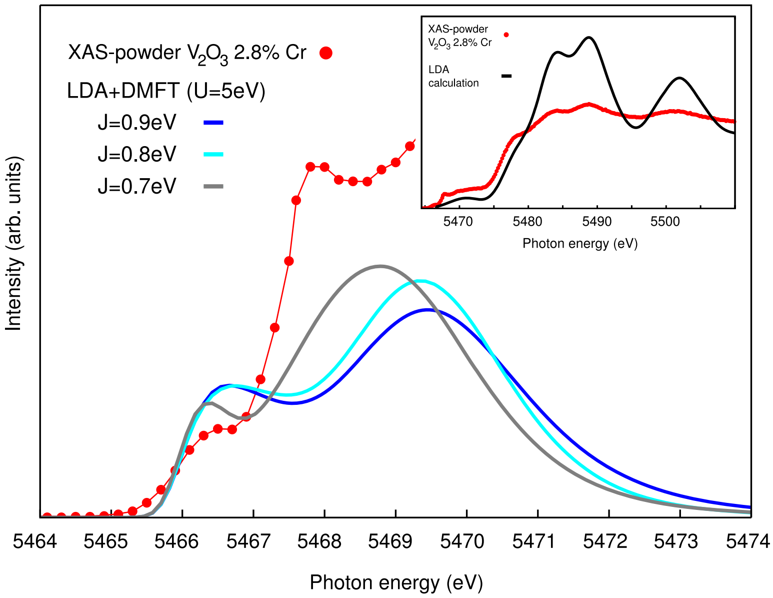

Figure 2. The V K pre-edge region compared to LDA+DMFT calculations. In the inset, the comparison of the whole edge with simple LDA results.

On the basis of previous work, [22, 23] the appearance of other features before peak A has been subject of debate: after extensive and repeated measurements, we were never able to detect any feature before peak A for neither the PM nor the PI phase. The main edge (including features D and E) corresponds to $1s \rightarrow 4p$ dipolar transitions, while in the pre-edge region $1s \rightarrow 3d$ quadrupolar transition play a major role: since the physics of the phase transitions in V_2O_3 is mainly determined by V $3d$ electrons, the pre-edge presents a special interest for our investigations. At the same time, the interpretation of XAS spectra in this region turns out to be especially difficult using conventional approaches.

In Fig. 2 (inset) we present the direct comparison between one of our experimental XAS spectra and the theoretical simulation obtained with the LDA based WIEN2k code: as one can see, if auto-absorption effects are taken into account, the agreement is quite satisfactory on the main edge where, consistently with previous work [24] the position of all main features is correctly reproduced. Concerning the pre-edge, instead, none of the main features (A, B and C) can be found as the result of LDA calculations, which cannot capture the rearrangement of the electronic levels caused by strong correlations.

A good agreement can be instead successfully achieved using a LDA+DMFT approach: in particular, it can be seen that peaks A and B are the spectroscopic signature of the split UHB. We fix the electron-electron interaction energy U to a value of 5 eV and fit the shape of the XAS pre-edge. This turns out to be a powerful method to determine the value of the Hund's coupling J, which in a Kanamori Hamiltonian description determines the splitting of the UHB. In Fig. 2 we show the detail of the experimental pre-edge compared with LDA+DMFT calculations for various values of J: as one can see, the energy difference between peaks A and B (about 1.7 eV) allowed us to set an upper limit of 0.7 eV for J, which is lower that what has been usually assumed in previous studies. Further improvements can be envisioned for our DMFT calculations, like the use of pairs of V atoms [25] rather than a single site: but with our results we can already confirm that, as already shown for other transition metal oxides [26, 27, 28], pre-K edge XAS represents a powerful method to extract information on the incoherent electronic

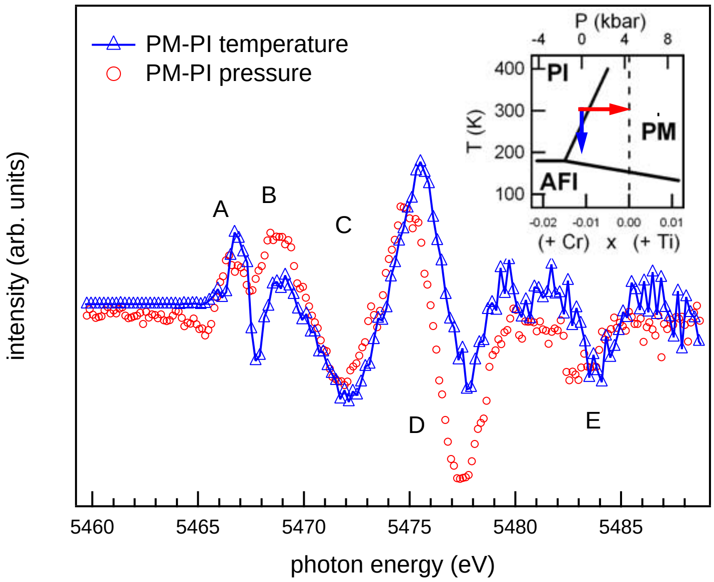

Figure 3. Differences of the V K edge XAS spectra between the PM and PI phases of $(V_{1-x}Cr_x)_2O_3$ for transitions induced by temperature (blue triangles) and pressure (red circles).

states of strongly correlated materials. Furthermore, if one compares the PM and PI phases in Fig. 1, one can also observe that no other features are present for the PM phase before peak A, meaning that the quasiparticle states close to the Fermi energy do not give a XAS spectroscopic signal, due to the effects of the core hole which disrupt the coherent density of states.

We have thus demonstrated that K-edge XAS, interpreted by means of LDA+DMFT calculations, makes it possible to describe the UHB of V_2O_3. As such, it can represent a powerful method to follow the evolution of the electronic structure over the whole phase diagram of this prototype material. In particular, the possibility of performing XAS measurements applying an external pressure represents an important tool for the study of electron-electron correlations: in fact, applying an external pressure represents a way of modifying them in a controlled way, by slightly reducing the interatomic distances and consequently increasing the wavefunction overlap.

The feasibility of this study is shown in Fig. 3, where the Mott transition in V_2O_3 is induced both by applying external pressure or varying the temperature. The spectroscopic differences between PM and PI are presented: in particular, the curve corresponding to the T induced transition is the same as the one presented in Fig. 1, in the spectral region where the most interesting features (A-E) are present. As explained before, the curve obtained under pressure was taken with poorer experimental resolution, so that the differences are less pronounced. Nevertheless, we can clearly see that applying an external pressure we can observe the same main changes due to the PM-PI phase transition, showing the strength of this method for the study of strongly correlated systems. Along with the overall similarity, it is precisely the study of the small differences (in particular in the spectral regions A and B) between these two curves which represents an interesting but also challenging problem. A more extensive set of measurements under pressure, performed with improved energy resolution, allowed us to explore the whole phase diagram while changing Cr doping level, temperature and pressure[29], thus providing deeper insight into the mechanisms governing the Mott transition in this protoype system.

5. Conclusion

We showed that K-edge XAS can be successfully employed to study correlation-driven phase transitions. LDA+DMFT was employed to interpret the differences in the V pre K-edge of vanadium sesquioxide at its isostructural PM-PI transition. Thanks to this combined experimental and theoretical effort, a more precise description was obtained of the split upper Hubbard band of this material, and a quantitative value was determined for its Hund coupling constant. The possibility of inducing the same transition under external pressure was also demontrated, offering the opportunity for more detailed studies over the whole (P,T) phase diagram which can be of great interest for our understanding of strongly correlated systems.

Acknowledgments

The financial support of a BQR of the Université Paris-Sud, of the Triangle de la Physique and of the Austrian Science Fund (FWF) are gratefully acknowledged.

References

[1] E. Dagotto, Science **309**, 257 (2005).
[2] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[3] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[4] D. B. McWhan and J. P. Remeika, Phys. Rev. B **2**, 3734 (1970).
[5] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice, Phys. Rev. B **7**, 1920 (1973).
[6] C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B **18**, 4945 (1978); Phys. Rev. B **18**, 4967 (1978); Phys. Rev. B **18**, 5001(1978).
[7] K. Held, I. Nekrasov, N. Blümer, V. Anisimov, and D. Vollhardt, Int. J. Mod. Phys. B **15**, 2611 (2001).
[8] I. S. Elfimov, N. A. Skorikov, V. I. Anisimov, and G. A. Sawatzky, Phys. Rev. Lett. **88**, 015504 (2002).
[9] G. Keller, K. Held, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. B **70**, 205116 (2004).
[10] 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).
[11] M. S. Laad, L. Craco, and E. Muller-Hartmann, Phys. Rev. B **73**, 045109 (pages 15) (2006).
[12] A. Tanaka, J. Phys. Soc. Jpn. **71**, 1091 (2002).
[13] J. M. Tomczak, and S. Biermann, Europhys. Lett. **86**, 37004 (2009).
[14] 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).
[15] P. Limelette, A. Georges, D. Jérome, P. Wzietek, P. Metcalf, and J. M. Honig, Science **302**, 89 (2003).
[16] 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, et al., Phys. Rev. Lett. **90**, 186403 (2003).
[17] S.-K. Mo, H.-D. Kim, J. D. Denlinger, J. W. Allen, J.-H. Park, A. Sekiyama, A. Yamasaki, S. Suga, Y. Saitoh, T. Muro, et al., Phys. Rev. B **74**, 165101 (2006).
[18] F. Rodolakis, B. Mansart, E. Papalazarou, S. Gorovikov, P. Vilmercati, L. Petaccia, A. Goldoni, J.-P. Rueff, S. Lupi, P. Metcalf, and M. Marsi , Phys. Rev. Lett. **102**, 066805 (2009).
[19] A.I. Frenkel, D.M. Pease, J.I. Budnick, P. Metcalf, E.A. Stern, P. Shanthakumar, and T. Huang, Phys. Rev. Lett. **97**, 195502 (2006).
[20] L. Baldassarre, A. Perucchi, D. Nicoletti, A. Toschi, G. Sangiovanni, K. Held, M. Capone, M. Ortolani, L. Malavasi, M. Marsi, et al., Phys. Rev. B **77**, 113107 (2008).
[21] R.O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
[22] A. Bianconi and C. R. Natoli, Solid State Communications **27**, 1177 (1978).
[23] J. Goulon, A. Rogalev, C. Goulon-Ginet, G. Benayoun, L. Paolasini, C. Brouder, C. Malgrange, and P. A. Metcalf, Phys. Rev. Lett. **85**, 4385 (2000).
[24] C. Meneghini, S. Di Matteo, C. Monesi, T. Neisius, L. Paolasini, S. Mobilio, C.R. Natoli, P.A. Metcalf and J.M. Honig, Phys. Rev. B **72**, 033111 (2005).
[25] S. Di Matteo, N.B. Perkins and C.R. Natoli, Phys. Rev. B **65**, 054413 (2002).
[26] A. Kotani, K. Okada, G. Vanko, G. Dhalenne, A. Revcolevschi, P. Giura and A. Shukla, Phys. Rev. B, **77**, 205116 (2008)
[27] C. Gougoussis, M. Calandra, A. Seitsonen, C. Brouder, A. Shukla, and F. Mauri, Phys. Rev. B **79**, 045118 (2009).
[28] F. de Groot, G. Vanko and P. Glatzel, J. Phys.: Condens. Matter, **21**, 104207 (2009)
[29] F. Rodolakis, P. Hansmann, J.-P. Rueff, A. Toschi, et. al., submitted.