Quasiparticles at the Mott Transition in V_2O_3: Wave Vector Dependence and Surface Attenuation

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We present an angle resolved photoemission study of V_2O_3, a prototype system for the observation of Mott transitions in correlated materials. We show that the spectral features corresponding to the quasiparticle peak in the metallic phase present a marked wave vector dependence, with a stronger intensity along the ΓZ direction. The analysis of their intensity for different probing depths shows the existence of a characteristic length scale for the attenuation of coherent electronic excitations at the surface. This length scale, which is larger than the thickness of the surface region as normally defined for noncorrelated electronic states, is found to increase when approaching the Mott transition. These results are in agreement with the behavior of quasiparticles at surfaces as predicted by Borghi *et al.* [Phys. Rev. Lett. **102**, 066806 (2009)].

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Collective electronic excitations are at the heart of many open issues in condensed matter physics, and present peculiar properties that are intrinsically different from those of the individual electrons that originate them. Mott-Hubbard systems, for instance, represent one well-known class of materials where small differences in the electronic structure close to the Fermi energy E_F, induced by electron correlations, produce spectacular macroscopic effects such as metal-insulator transitions [1]. In particular, the phase transition between the paramagnetic insulating (PI) and paramagnetic metallic (PM) phase in $(V_{1-x}Cr_x)_2O_3$ has attracted a lot of attention as a prototype case of Mott transition [2,3]. From the theoretical point of view, the advent of dynamical mean field theory (DMFT) [4,5] has allowed considerable progress in its description, providing a conceptual framework which predicts that the insulator to metal transition is characterized by a coherent quasiparticle peak developing between the incoherent Hubbard bands; on the experimental side, the observation of such peak in photoemission experiments on vanadium sesquioxide [6,7] has validated this physical picture, so that the appearance of a quasiparticle peak at E_F can really be regarded as the distinctive spectral feature of a correlated metal.

A complete understanding of this prototype Mott system requires more extensive experimental studies of its low energy electronic states, which can be, on the other hand, quite elusive: as pointed out by Mo *et al.* [6,7], only the increased bulk sensitivity of their high photon energy photoemission setup made it possible to detect a quasiparticle peak in the metallic phase of V_2O_3. Indeed, in many previous attempts [8–13] only a very limited amount of spectral weight had been detected at E_F, due to the intrinsic surface sensitivity of photoemission: in particular, no angle resolved photoemission (ARPES) data are available to describe the dispersion of the quasiparticle peak across the Brillouin zone. This situation reflects a general trend in strongly correlated materials—a surface layer presenting an insulating behavior while the bulk is metallic—which is normally attributed to the fact that at the surface electron correlation effects are more relevant [14]. On the other hand, if there is now consensus on the importance of using a bulk sensitive probe to explore the properties of vanadium sesquioxide as well as in general of strongly correlated materials [15,16], the problem of understanding what is specific to collective electronic excitations that makes the effects of the surface more pronounced requires further attention.

We present here an ARPES study of the low energy excitations in $(V_{1-x}Cr_x)_2O_3$ $(x = 0, 0.011)$ performed at low photon energy, i.e., in conditions that allow a reduced surface sensitivity [17] with respect to standard ARPES measurements [9,10], finding that the spectral weight contributing to the quasiparticle peak is more intense in certain points in $\mathbf{k}$ space along the ΓZ direction. This piece of information is important to check in a more detailed way quantitative theoretical models for this prototype system [18–20], and confirms the predictions of recent calculations combining local density approximation (LDA) with DMFT [21]. We found that the most intense quasiparticle signal could be obtained only combining the detection of the proper photoelectron momentum with maximum prob-

ing depth, and that the coherent part of the spectral function reacts to the presence of the surface differently from the other electronic states, over a length scale larger than the surface region as normally defined in surface science. This characteristic length—which appears to be the key to explain the peculiar behavior of quasiparticles at surfaces—is found to increase when approaching the Mott transition.

The experiments were performed on the BaD ElPh beam line at the Elettra synchrotron light source, using photons dispersed in the 5–26 eV range by a normal incidence monochromator. The photoelectrons were detected with a Phoibos 150 hemispherical analyzer. The overall instrumental resolution was better than 50 meV for the data presented here; the selected angular acceptance was typically 7° (corresponding to 0.14 Å^{-1} at 5 eV kinetic energy). High quality single crystals of $(V_{1-x}Cr_x)_2O_3$ were precisely oriented using Laue x-ray diffraction, cut in bars of approximately $4 \times 4 \times 10$ mm^3 in size, notched and cleaved in ultrahigh vacuum to obtain clean (102) [or $(10\bar{1}2)$ in extended hexagonal notation] and (001) surfaces. The quality of the hexagonal (001) surfaces was in the best cases comparable to those obtained exposing the (102) plane, which is normally used to fracture this compound, even though the percentage of successful cleaves was found to be lower. First tests on fresh (102) surfaces of $(V_{0.989}Cr_{0.011})_2O_3$ revealed a clear indication of the phase transition while cooling from 300 K (PI) to 200 K (PM) with the appearance of a stronger signal at E_F but, consistent with previous work [9,10], no pronounced quasiparticle peak could be observed.

We repeated the same procedure also by cleaving the specimens perpendicular to the [001] axis. With this choice, we were able to explore the high symmetry ΓZ direction by tuning the photon energy while detecting normal emission photoelectrons, which helped enhance as much as possible the bulk sensitivity of our measurements. Scanning the photon energy in the 7–21 eV range showed for the PM phase the most intense signal at E_F in a narrow window between 8 and 9 eV: this can be clearly seen in Fig. 1(a), where we present the spectra taken between 7 and 10 eV. In particular, a quasiparticle peak is clearly visible at about -0.25 eV binding energy, accompanied by the lower Hubbard band at about -1.2 eV. These values are in nice agreement with recent detailed theoretical predictions for the spectral functions along ΓZ [21]. The peak is most intense at 9 eV, which corresponds to a point on the ΓZ axis at 0.1 Å^{-1} distance from Γ (that we shall indicate as Ω), as estimated by using for the inner potential V_0 the value of 21.76 eV [22] already adopted in previous ARPES studies on V_2O_3 [9]. By testing several dispersive directions, we consistently found the intensity of the quasiparticle decreasing while moving away from Ω. We also notice that the PI phase showed an overall less pronounced momentum dependence, and that the comparison of the spectra at 9 eV at 300 and 200 K clearly shows

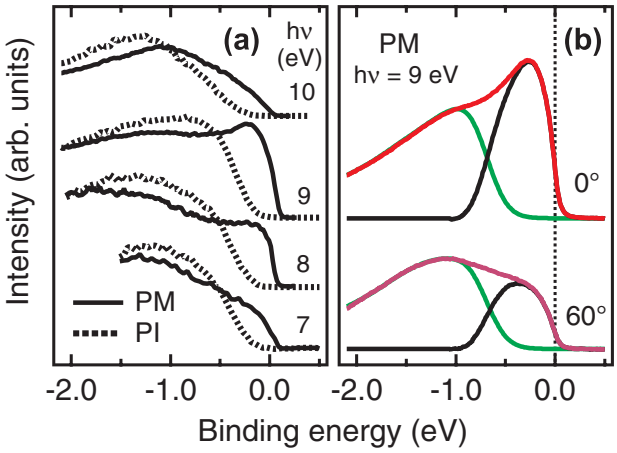

FIG. 1 (color online). (a) Normal emission photoelectron spectra taken at 300 K (PI) and 200 K (PM) from the (001) surface of $(V_{0.989}Cr_{0.011})_2O_3$. (b) Spectra taken at 300 K (PM) from the (001) surface of V_2O_3 at normal (0°) and grazing (60° from normal) photoelectron emission angle.

the typical behavior predicted for a Mott transition, with the appearance of a quasiparticle peak at E_F and a readjustment of the lower Hubbard band. However, the intensity of the coherent part of our experimental spectra is much weaker when compared to more bulk sensitive angle integrated photoemission results [6,7]. This can be clearly seen in Fig. 1(b), where we separate the contribution of the Hubbard band and of the quasiparticle peak to the total spectral function of undoped V_2O_3 (PM at room temperature), after subtraction of a Shirley-type experimental background. The line shapes for the two components were obtained by decomposing theoretical LDA + DMFT spectral functions [21] in a coherent and an incoherent part, and allowing their height and width to vary to fit our experimental spectra.

In order to further investigate this problem, we explored the angular dependence of the photoemission signal while changing the detection angle with respect to the surface normal. This approach has already been used by Mo *et al.* [7] using high energy photoemission, as one additional proof of the necessity of using a bulk sensitive probe to detect the quasiparticle: the angular resolution of our setup allowed us to extract some more specific information on the interplay between wave vector dependence and surface attenuation effects.

In Fig. 2 we present the results obtained on undoped V_2O_3 at 9 eV photon energy for the (102) [Fig. 2(a)] and the (001) surface [Fig. 2(b)]. For the former, the c axis is at 58.5° from the surface normal, thus emission from the ΓZ direction is obtained around this angle of detection; for the latter, it corresponds to normal photoelectron emission as explained above. Using these two surface orientations, it is possible to probe the band dispersion while moving away from Ω in $\mathbf{k}$ space with two different levels of surface sensitivity: if μ is the inelastic mean free path of the photoelectrons, on the (001) surface we detect photoelectrons

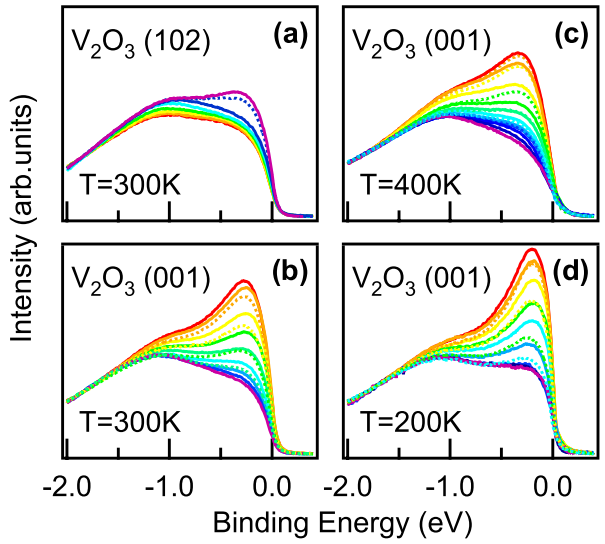

FIG. 2 (color online). Angular dependence of the background subtracted photoemission yield at $h\nu = 9$ eV [from normal to grazing emission corresponds to spectra from red to violet, i.e., from bottom to top in (a) and from top to bottom in (b)–(d)]; the top spectra always correspond to emission from ΓZ.

from Ω with a probing depth determined by μ, while on the (102) surface it will be determined by $\mu\cos(58.5°) \sim \mu/2$; the opposite will be true for the spectra farthest away from Ω, on the other extreme of our angular scans.

One can immediately observe the similarity of the behavior of the dispersion of the Hubbard band (slight dispersion of about 0.2 eV while moving away from Ω) and the striking difference in the behavior of the quasiparticle peak, in terms of intensity with respect to the Hubbard band itself. The degree of surface sensitivity of our probe does not affect the coherent peak height with respect to the Hubbard band for points far away from Ω, while it makes a strong difference when the coherent density of states is high: this can be seen by comparing the violet spectra [top one in Fig. 2(a) and bottom one in Fig. 2(b)], corresponding to more grazing emission around 58.5°, with the red spectra [bottom one in Fig. 2(a) and top one in Fig. 2(b)], corresponding to normal emission. The intensity of the quasiparticle is always the most pronounced at Ω, but it is strongly attenuated when detected in a more surface sensitive fashion (i.e., grazing photoelectron emission); the lower Hubbard band, instead, shows a remarkably similar behavior, irrespective of the more or less surface sensitive acquisition mode [see also Fig. 1(b)].

All these observations suggest that the effects of the surface on the incoherent band electronic structure take place over a depth which is smaller than our μ, and this depth can be regarded as the thickness of the surface region as normally defined in surface science—a region where atoms are arranged differently and consequently the electronic bands are different with respect to the bulk. The coherent states, instead, are attenuated over a larger scale, at least as large as the mean free path μ for the electrons we are detecting. Otherwise said, coherent electronic states in our correlated metal react to the presence of a surface over a length scale which is larger than the thickness of the surface region itself. Consequently, this length scale should be determined by the bulk properties of the strongly correlated material.

Estimating this characteristic length on the basis of our results would require a precise knowledge of μ. The values of the photoelectron mean free path are not well known at low kinetic energies: for the range of photoelectron energies used in this work, Miller *et al.* [23] determined a μ of 30 Å for a metal (Ag), while more recently smaller values have been estimated for an insulating oxide [24]. Furthermore, an assumption needs to be made on the profile of the quasiparticle weight versus the distance from the surface. No specific predictions exist to describe this profile for vanadium sesquioxide, but single band Hubbard models have been used to explore the effects of the surface in a generic correlated metal [25]. Borghi *et al.* [26] derive an exponential scaling law that can result in a quasiparticle weight approaching the surface with upward curvature, which seems to be more consistent with the attenuation behavior presented in Fig. 2. Based on these considerations, we can estimate that for V_2O_3 at least 40 Å are needed for the quasiparticle to reach its bulk intensity.

To get more insight on the properties of this attenuation layer, we also explored the behavior of the quasiparticle weight in different parts of the V_2O_3 phase diagram. In Fig. 2 we also present its angular dependence for the (001) surface at 400 K [Fig. 2(c)] and 200 K [Fig. 2(d)]. With respect to the 300 K spectra in Fig. 2(b), the coherent features become broader at higher temperature and sharper at low temperature, which is well consistent with the expected transfer of spectral weight for correlated metals. The way the quasiparticle vanishes at the surface, though, evolves in a different way: in Fig. 3 we present the variation with the detection angle of the spectral weight of the

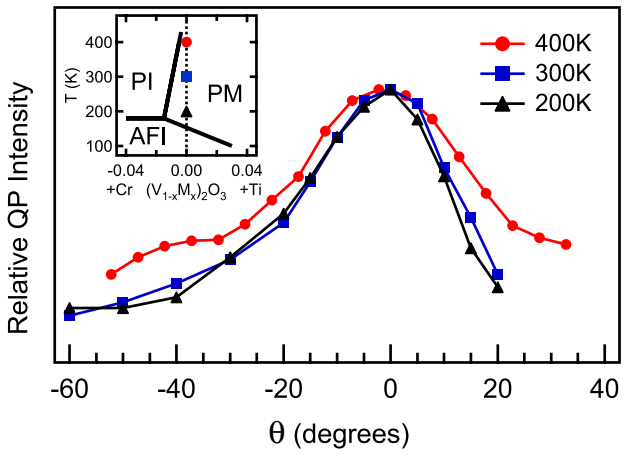

FIG. 3 (color online). Angular attenuation of the quasiparticle weight. The data points correspond to the spectra in Figs. 2(b)–2(d). The curves were normalized to their values at normal emission.

quasiparticle peak relative to the lower Hubbard band. The curves have been normalized to their normal emission values in order to make it easier to compare the vanishing behavior of the quasiparticle in the three different cases. The angular dependence is only slightly slower at 300 K with respect to 200 K, while it is considerably less pronounced at 400 K. Of course, both wave vector effects and surface attenuation contribute to this angular dependence: in particular, its asymmetric behavior with respect to the detection angle is due to dispersion effects. Its evolution with temperature, instead, can only be due to surface attenuation, since the band structure is not expected to change with temperature: as pointed out in a recent infrared spectroscopy study [27], the quasiparticle weight presents a continuous evolution until 425 K, before entering the crossover region at 450 K, where a small discontinuous structural change occurs which amplifies the correlation effects opening a pseudogap in the optical conductivity. Thus, we can conclude that the different angular response of the photoelectron yield at 400 K is not related to the temperature *per se*, but rather to the parametric position in the phase diagram. The proximity to the crossover region, where the quasiparticle becomes incoherent, may contribute to this peculiar behavior. Furthermore, it should be noted that the point at 400 K is very close to the PI/PM transition (inset of Fig. 3), while the points at 300 K and, even more, at 200 K are already far away from it. This observation is in nice agreement with the model proposed by Borghi *et al.* [26]: they predict a diverging behavior for the characteristic length of the surface dead layer when approaching the Mott transition, which in our case means a less pronounced angular variation of the quasiparticle photoemission yield.

In conclusion, we studied the variation across the Brillouin zone of the weight of the quasiparticle peak in the metallic phase of the prototype Mott-Hubbard system V_2O_3, and we identified a momentum region on the ΓZ direction where this weight is strongest. The transition to the insulating phase shows the characteristic features of a correlation induced Mott transition, where the coherent quasiparticle disappears while the incoherent Hubbard bands readjust. We also studied in detail the vanishing behavior of the quasiparticle peak at the surface, where the coherent features fade away while the incoherent bands are not affected. This effect, which contributes to the angle resolved photoemission yield together with genuine band dispersion effects, shows that the coherent correlated electronic states react to the presence of the surface with a characteristic length which seems to be an intrinsic bulk property of the system. Our results show that this intrinsic length increases in the proximity of a Mott instability, as predicted by Borghi *et al.* in the following Letter [26]. The existence of such an intrinsic length should be in our opinion a general property of coherent low energy electronic states, playing an important role in the many phenomena that take place at the interface between correlated materials, as well as in our overall understanding of these systems.

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[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990).
[2] D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Lett. **23**, 1384 (1969).
[3] D. B. McWhan and J. P. Remeika, Phys. Rev. B **2**, 3734 (1970).
[4] W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989).
[5] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[6] S.-K. Mo *et al.*, Phys. Rev. Lett. **90**, 186403 (2003).
[7] S.-K. Mo *et al.*, Phys. Rev. B **74**, 165101 (2006).
[8] G. A. Sawatzky and D. Post, Phys. Rev. B **20**, 1546 (1979).
[9] K. E. Smith and V. E. Henrich, Phys. Rev. B **38**, 5965 (1988).
[10] K. E. Smith and V. E. Henrich, Phys. Rev. B **50**, 1382 (1994).
[11] S. Shin *et al.*, J. Phys. Soc. Jpn. **64**, 1230 (1995).
[12] H.-D. Kim *et al.*, Phys. Rev. B **57**, 1316 (1998).
[13] R. Zimmermann, R. Claessen, F. Reinert, P. Steiner, and S. Hufner, J. Phys. Condens. Matter **10**, 5697 (1998).
[14] K. Maiti, P. Mahadevan, and D. D. Sarma, Phys. Rev. Lett. **80**, 2885 (1998).
[15] G. Panaccione *et al.*, Phys. Rev. Lett. **97**, 116401 (2006).
[16] A. Sekiyama, T. Iwasaki, K. Matsuda, Y. Saitoh, Y. Onuki, and S. Suga, Nature (London) **403**, 396 (2000).
[17] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).
[18] K. Held, G. Keller, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. Lett. **86**, 5345 (2001).
[19] G. Keller, K. Held, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. B **70**, 205116 (2004).
[20] M. S. Laad, L. Craco, and E. Müller-Hartmann, Phys. Rev. B **73**, 045109 (2006).
[21] 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).
[22] J. Ashkenazi and T. C. Chuchen, Philos. Mag. **32**, 763 (1975).
[23] T. Miller, W. E. McMahon, and T.-C. Chiang, Phys. Rev. Lett. **77**, 1167 (1996).
[24] F. Offi *et al.*, Phys. Rev. B **77**, 201101 (2008).
[25] M. Potthoff and W. Nolting, Phys. Rev. B **60**, 7834 (1999).
[26] G. Borghi, M. Fabrizio, and E. Tosatti, following Letter, Phys. Rev. Lett. **102**, 066806 (2009).
[27] L. Baldassarre *et al.*, Phys. Rev. B **77**, 113107 (2008).