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Prominent Quasiparticle Peak in the Photoemission Spectrum of the Metallic Phase of V_2O_3

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We present the first observation of a prominent quasiparticle peak in the photoemission spectrum of the metallic phase of V_2O_3 and report new spectral calculations that combine the local-density approximation with the dynamical mean-field theory (using quantum Monte Carlo simulations) to show the development of such a distinct peak with decreasing temperature. The experimental peak width and weight are significantly larger than in the theory.

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$(V_{1-x}Cr_x)_2O_3$ displays a complex phase diagram with paramagnetic metal (PM), paramagnetic insulator (PI), and antiferromagnetic insulator (AFI) regions. The PM to PI transition serves as the paradigm of the Mott-Hubbard (MH) metal-insulator transition (MIT) [1]. The MH scenario for $(V_{1-x}Cr_x)_2O_3$ was put forth originally in the context of the half-filled one-band Hubbard model in which the tendency of the on-site Coulomb repulsion "U" to make a correlation gap insulator competes with the tendency of site to site hopping to make a broad band metal of bandwidth "B." A coherent thermodynamically consistent description of the MIT became possible with the development of the dynamical mean-field theory (DMFT) [2]. DMFT describes the strongly interacting metal in terms of Fermi liquid quasiparticles, i.e., single particle excitations near the Fermi energy E_F which remain well defined as in a noninteracting system but have a self-energy correction that increases their effective mass and reduces their spectral weight. In application to the Hubbard model, DMFT is significant as the best description that can be made by using a local (i.e., independent of momentum $\mathbf{k}$) self-energy. It may be formulated as a mapping of the lattice problem onto an effective Anderson impurity model coupled self-consistently to an effective conduction band bath [3]. In the metallic phase, although the large U value acts to separate much of the band's spectral weight away from E_F into the so-called upper and lower Hubbard bands, there remains at E_F a distinctive quasiparticle (QP) peak, not accidentally reminiscent of the Kondo/Suhl-Abrikosov resonance [4] of the Anderson impurity model. The weight of the QP-peak decreases with increasing U/B and goes to zero at a critical value of U/B, which thus marks the MIT.

Such a distinctive peak could in principle be seen in photoemission spectroscopy (PES). However, in spite of continuing efforts for over 20 years, literature [5–10] V $3d$ PES spectra for the PM phase of $(V_{1-x}Cr_x)_2O_3$ have shown at most a near E_F feature that is the smallest part of the spectrum. One could hypothesize that the distinctive central peak of the half-filled one-band model is obscured and washed out by the multiband complexity of the actual electronic structure of $(V_{1-x}Cr_x)_2O_3$ in which the two $3d$ electrons of the V^{3+} ion must be distributed among singly degenerate a_{1g} and doubly degenerate e_g^{π} orbitals derived from a small trigonal crystal field splitting of the cubic t_{2g} manifold of the V $3d$ states. Indeed, recent experiment [11] and theory [12] establishing an $S = 1$ state for the V^{3+} ions show that such a multiband description is essential. Further, a recent study that included these material specific aspects by combining the local-density approximations with DMFT (using quantum Monte Carlo simulations) [LDA + DMFT (QMC)] [13] found for the PM phase a weak E_F peak in good agreement with that of a well resolved and high quality PM phase spectrum by Schramme *et al.* [14], taken at a photon energy ($h\nu$) of 60 eV. However, it is important to note that numerical complexities constrained the calculation to be performed at a temperature

T of 1160 K, whereas the photoemission spectrum was obtained at a much lower temperature of 300 K, and that for the photon energy used, recent PES studies of other vanadium oxides have been found [15,16] to yield spectra not characteristic of the bulk, but rather of the surface atoms whose lower coordination number reduces B proportionately and thus can render the surface layer much more strongly correlated or even insulating. Both circumstances go in the direction of a greatly reduced QP peak.

In this Letter we report angle-integrated PES spectra for the metallic phase of V_2O_3 that are different from all previous spectra in showing an E_F peak whose amplitude exceeds that of the rest of the V $3d$ spectrum by a factor approaching 2. These results were achieved by measuring at high photon energies in order to increase the bulk sensitivity but with much better resolution [17] than in previous [10,18] studies at these energies. Equally important is the use of a small photon spot (≈ 100 μm diameter) that we have found [19] to be essential for minimizing the effects of steps and other roughness that can be seen in high resolution optical micrographs of typical cleaved single crystal surfaces of this material. Doing so is very important because atoms with the edge and corner (i.e., acute) geometries of steps and general roughness have coordinations that are reduced from those of the planar surface atoms. Concomitantly, as is known from past theory [20] and experiment [21] on correlated electron materials, they have even larger differences from the electronic structure of the bulk than occurs for the planar surface atoms. The large amplitude of the newly observed peak disagrees with the theory of Ref. [13]. However, we also report new LDA + DMFT (QMC) calculations for the same electronic structure and U value as previously [13], showing that with temperature decreasing to 300 K such a prominent central peak develops. Nonetheless, the quantitative comparison enabled by the new experiment and new theory reveals important differences.

PES using circularly polarized photons with $h\nu$ between 310 and 700 eV was performed at the twin-helical undulator beam line BL25SU [22] of SPring-8 equipped with a SCIENTA SES200 analyzer and giving a photon spot size of diameter 100 μm. The Fermi level and overall energy resolution (≈ 90 to 170 meV over the $h\nu$ range) were determined from the Fermi-edge spectrum of a Pd metal reference. Well annealed oriented single-crystalline samples of V_2O_3 were cleaved to expose a hexagonal $(10\bar{1}2)$ plane in a vacuum of 2×10^{-10} Torr. Using a closed-cycle He cryostat and an embedded resistive heater, the sample temperature was held at $T =$ 175 K, somewhat above the PM/AFI transition. Surface integrity was well maintained under the vacuum and photon exposure, as shown by the repeatability of the spectra for at least 10 hours after cleaving, after which the PM/AFI transition could still be observed in the spectra at the temperature appropriate for stoichiometric V_2O_3. The inset of Fig. 1 shows a cross section of the

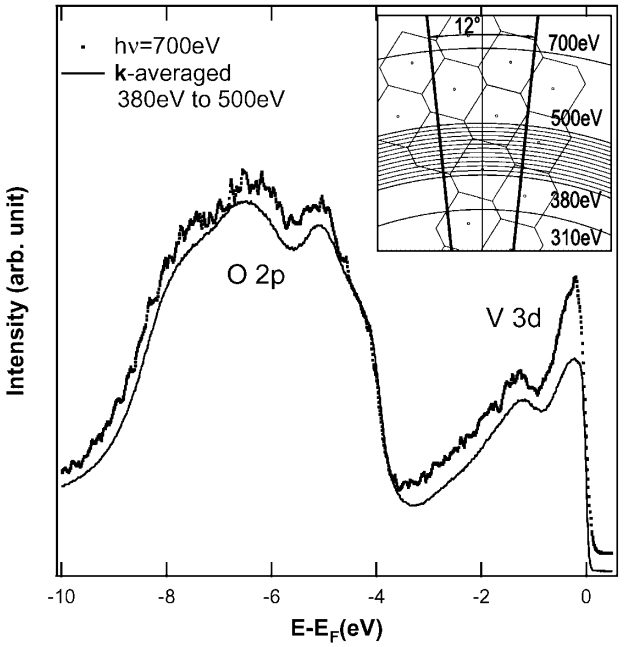

FIG. 1. $h\nu = 700$ eV and **k**-averaged PES spectra of V_2O_3. The inset shows the **k** space covered by the detector angular acceptance for various $h\nu$.

k-space Brillouin zone stacking normal to the cleavage plane and also the spherical surfaces [23] traversed as the detector angles are varied about the normal for various fixed $h\nu$ between 310 eV and 700 V. Radial lines show the **k** range corresponding to the analyzer acceptance angle of about $\pm 6°$. This range is ± 1.2 Å^{-1} for a photoelectron with 500 eV kinetic energy and covers more than one Brillouin zone for any $h\nu$ arc.

The $h\nu = 700$ eV spectrum of Fig. 1 shows the general character of the data. The V $3d$ emission is well separated from the O $2p$ emission, and the newly observed prominent E_F peak is very obvious. We are interested here in the $h\nu$ dependence of the spectral shape of the V $3d$ emission. Although there is a huge $3d$ enhancement over the range 510 to 560 eV, due to a $3d$ cross-section resonance at the V $2p$ edge [10,18], we have deliberately avoided the resonance region because we have found [24] in this range incoherent Auger emission that distorts the spectral shape. Because we make comparisons to a **k**-summed theory, Fig. 1 also shows the result of **k** averaging across a full Brillouin zone by using spectra taken in 10 eV steps from 380 to 500 eV. The E_F peak in the **k**-averaged spectrum is somewhat smaller than that in the 700 eV spectrum. This is, however, due to the reduced bulk sensitivity of the lower photon energies rather than the **k** selectivity of the single photon energy, as discussed next.

Figure 2 shows our V $3d$ spectra for $h\nu$ from 310 to 700 eV along with the $h\nu = 60$ eV spectrum [14] that was found to compare favorably to the 1160 K theory spectrum in Ref. [13]. A Shirley-type inelastic background has been removed in an identical way [25] for each spectrum. The spectra are normalized over the range

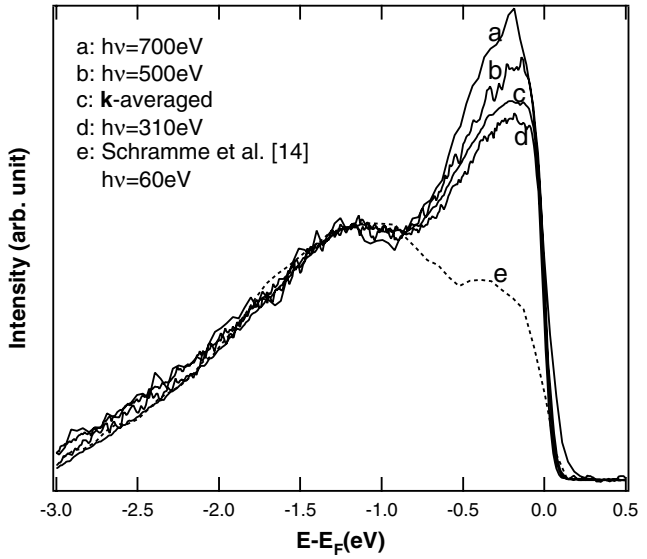

FIG. 2. PES spectra taken with various $h\nu$, the largest of which yields the greatest bulk sensitivity.

below -1 eV for ease of comparing their E_F peaks. Relative to the spectrum below -1 eV, the E_F peaks in the spectra of Fig. 2 increase monotonically with increasing $h\nu$. Over the range for the **k**-averaged spectrum the peak is never larger than at 500 eV. Although some nonmonotonic variation over this range and also below 300 eV (not shown) could signal **k** dependence, we conclude that above 300 eV the change of probe depth dominates **k**-dependent effects in the data. This conclusion is reinforced by the observation at 500 eV that rotating the detection angle away from the normal in steps of 15° out to 60°, which monotonically decreases the effective probe depth, monotonically decreases the E_F peak to be comparable to the E_F feature that is seen in the 60 eV data. Reliably estimating a bulk spectrum from the $h\nu$ and angle dependences using various phenomenological models is not simple. We will present such estimates in a more detailed paper. However, the results do not differ from the 700 eV spectrum itself in any way that is significant for the comparison to new theory that we make next.

On the theoretical side, new, very CPU-intensive LDA + DMFT (QMC) calculations have been made at considerably lower temperatures than previously [13], i.e., $T = 700$ and 300 K, in exactly the same manner [26] as before. The LDA density of states of the three t_{2g} bands at the Fermi energy was identified with a one-particle Hamiltonian which was supplemented by a local Coulomb interaction $U = 5$ eV (only U values close to 5 eV generate the experimentally observed MIT upon Cr doping [13]) and a Hund's rule coupling $J = 0.93$ eV (according to constrained LDA calculations [27]). This three-band many-body problem was solved by DMFT using QMC simulations.

Figure 3 shows our theory spectra for three temperatures, compared to the experimental $h\nu = 60$ eV spectrum (300 K) and the 700 eV spectrum (175 K) of Fig. 2, all scaled to have equal areas. The theory curves include the Fermi function for the appropriate temperature and Gaussian broadening of 90 meV to simulate experimental resolution. Qualitatively similar to the behavior of the impurity model's Kondo resonance [4], at higher temperatures the QP peak is greatly broadened by thermal occupation of states bearing local magnetic moments. As the system settles with decreasing temperature toward its nonmagnetic ground state, the peak sharpens, its amplitude increases strongly, and it becomes clearly separated from the lower Hubbard band at about -1.25 eV. These temperature-induced changes strongly enhance the differences between theory and experiment that were already present but small in Ref. [13]; i.e., the amplitude of the QP peak is much larger in the theory than in the $h\nu = 60$ eV experimental spectrum. Qualitatively, the comparison to the new bulk sensitive spectrum is much better, with the prominent QP peak and the lower Hubbard band of the theory being very similar, respectively, to the newly observed E_F peak and the broad hump centered at -1.25 eV. Strikingly different, however, are that the experimental E_F peak is broader and also has more spectral weight. These differences will persist for theory at the slightly lower temperature of the data. The width difference could increase somewhat. The weight difference would decrease but probably not greatly. From 1160 to 300 K the theory peak's integrated spectral weight, taken as that above -0.63 eV, increases by only 11%.

Within the DMFT scheme the larger experimental width and weight implies weaker correlation that could be described by using a reduced U value. However, in the

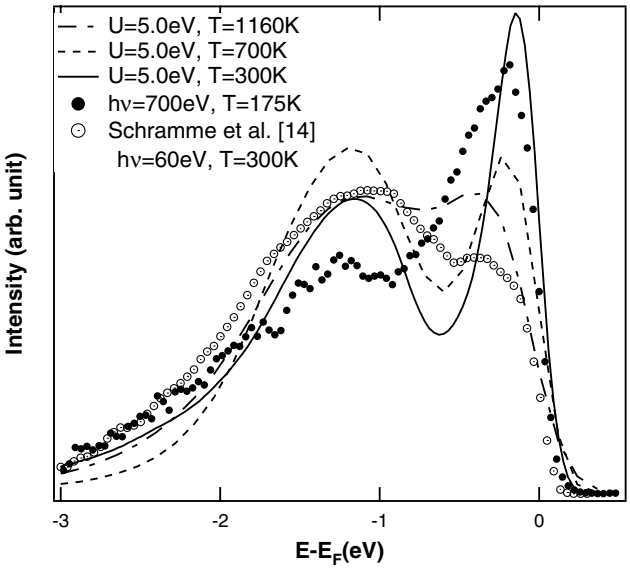

FIG. 3. LDA + DMFT (QMC) calculations made at three temperatures for $U = 5.0$ eV, the $h\nu = 60$ eV PES spectrum [14] compared to theory in Ref. [13], and our new $h\nu = 700$ eV bulk sensitive spectrum.

present theory [13] the MIT under Cr doping would not occur for such a reduced U value unless U then increases with Cr doping or through the MIT transition. Either might be expected to occur through reduction in various effective screening processes, some of which are excluded from the present theory by its restriction to three bands. Another possible origin for the increased width of the experimental peak is the **k** dependence of the single particle self-energy. This is beyond our current calculations, but may partly be included by an improved DMFT calculation which uses a pair of V ions [28] instead of a single site.

In summary, we have discovered a prominent E_F peak in the PES spectrum of V_2O_3 in the PM phase, at a temperature somewhat above that of the AFI phase transition. New LDA + DMFT (QMC) theory for a comparable temperature also finds such a prominent QP peak, generic to the DMFT theory of the Hubbard model near the MIT transition. The quantitative comparison that is enabled by the two new results reveals significant differences that must be addressed in future work. Nonetheless, considering the various approximations of the present theory, the comparison is very encouraging as to the occurrence of the basic QP peak that is central to the DMFT description.

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[1] N. F. Mott, Rev. Mod. Phys. **40**, 677 (1968); *Metal-Insulator Transitions* (Taylor & Francis, London, 1990); F. Gebhard, *The Mott Metal-Insulator Transition* (Springer, Berlin, 1997).
[2] W. Metzner and D. Vollhardt, Phys. Rev. Lett. **62**, 324 (1989); A. Georges *et al.*, Rev. Mod. Phys. **68**, 13 (1996).
[3] A. Georges and G. Kotliar, Phys. Rev. B **45**, 6479 (1992); M. Jarrell, Phys. Rev. Lett. **69**, 168 (1992).
[4] O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, p. 103.
[5] G. A. Sawatzky and D. Post, Phys. Rev. B **20**, 1546 (1979).
[6] K. E. Smith and V. E. Henrich, Phys. Rev. B **38**, 5965 (1988).
[7] K. E. Smith and V. E. Henrich, Phys. Rev. B **50**, 1382 (1994).
[8] S. Shin *et al.*, J. Phys. Soc. Jpn. **64**, 1230 (1995).
[9] H.-D. Kim *et al.*, Phys. Rev. B **57**, 1316 (1998).
[10] R. Zimmermann *et al.*, J. Phys. Condens. Matter **10**, 5697 (1998).
[11] J.-H. Park *et al.*, Phys. Rev. B **61**, 11 506 (2000).
[12] S. Yu. Ezhov *et al.*, Phys. Rev. Lett. **83**, 4136 (1999).
[13] K. Held *et al.*, Phys. Rev. Lett. **86**, 5345 (2001).
[14] M. Schramme, Ph.D. thesis, Universität Augsburg, 2000; M. Schramme *et al.* (unpublished).
[15] K. Maiti, P. Mahadevan, and D. D. Sarma, Phys. Rev. Lett. **80**, 2885 (1998).
[16] A. Sekiyama *et al.*, cond-mat/0206471.
[17] A. Sekiyama *et al.*, Nature (London) **403**, 396 (2000).
[18] J.-H. Park, Ph.D. thesis, University of Michigan, 1994.
[19] Our initial high $h\nu$ work, unpublished, but reported in cond-mat/0108044, employed a photon spot size of ≈ 1 mm diameter. The importance of a small spot size was discovered in subsequent exploratory studies made with lower energy resolution on the spectromicroscopy beamline 7.0 at the ALS.
[20] B. Johansson, Phys. Rev. B **19**, 6615 (1979).
[21] M. Domke *et al.*, Phys. Rev. Lett. **56**, 1287 (1986).
[22] Y. Saitoh *et al.*, Rev. Sci. Instrum. **71**, 3254 (2000).
[23] Following Ref. [6] the figure is drawn for an inner potential of 21.76 eV, but, in fact, there is negligible dependence on the inner potential value for these large $h\nu$.
[24] The overlapping Auger emission was discovered after our initial (cond-mat/0108044) high $h\nu$ work. Although not intense, it nonetheless distorts the line shape to peak somewhat below E_F.
[25] The background brings the spectra to zero at the minimum between the V $3d$ and O $2p$ regions, implicitly making a separation between the two.
[26] More details and a pedagogical introduction are given in K. Held *et al.*, in *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, edited by J. Grotendorst, D. Marks, and A. Muramatsu, NIC Series Vol. 10 (John von Neumann Institute for Computing, Julich, Germany, 2002), pp. 175–209.
[27] I. Solovyev *et al.*, Phys. Rev. B **53**, 7158 (1996).
[28] Past and recent discussion of pair models is given in J.W. Allen, Phys. Rev. Lett. **36**, 1249 (1976); F. Mila *et al.*, Phys. Rev. Lett. **85**, 1714 (2000); S. di Matteo *et al.*, Phys. Rev. B **65**, 054413 (2002).