Hubbard band or oxygen vacancy states in the correlated electron metal SrVO$_3$?

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We study the effect of oxygen vacancies on the electronic structure of the model strongly correlated metal SrVO$_3$. By means of angle-resolved photoemission (ARPES) synchrotron experiments, we investigate the systematic effect of the UV dose on the measured spectra. We observe the onset of a spurious dose-dependent prominent peak at an energy range where the lower Hubbard band has been previously reported in this compound, raising questions on its previous interpretation. By a careful analysis of the dose dependent effects we succeed in disentangling the contributions coming from the oxygen vacancy states and from the lower Hubbard band. We obtain the intrinsic ARPES spectrum for the zero-vacancy limit, where a clear signal of a lower Hubbard band remains. We support our study by means of state-of-the-art ab initio calculations that include correlation effects and the presence of oxygen vacancies. Our results underscore the relevance of potential spurious states affecting ARPES experiments in correlated metals, which are associated to the ubiquitous oxygen vacancies as extensively reported in the context of a two-dimensional electron gas (2DEG) at the surface of insulating $d^0$ transition metal oxides.

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A major challenge of modern physics is to understand the fascinating phenomena in strongly-correlated transition metal oxides (TMOs), which emerge in the neighborhood of the Mott insulator state. Some preeminent examples that have gathered the interest for almost 30 years are high temperature superconductivity, colossal magnetoresistance, heavy fermion physics and, of course, the Mott metal-insulator transition itself [1]. Significant theoretical progress was made with the introduction of Dynamical Mean Field Theory (DMFT) and its combination with ab initio Density Functional methods (LDA+DMFT), which allows treatment of the interactions promoting itinerancy and localization of electrons on equal footing [2,4]. Among the most emblematic achievements of DMFT is the prediction of a Hubbard satellite, which splits off of the conduction band of a metal. This satellite results from the partial localization of conduction electrons due to their mutual Coulomb repulsion. Early DMFT studies also showed that it is the precursor of the localized electronic states of a Mott insulator [5]. Since then, these predictions promoted a large number of studies using photoemission spectroscopy, which is a technique to directly probe the presence of Hubbard bands. In this context, the TMO system SrVO$_3$ has emerged as the drosophila model system to test the predictions of strongly correlated electron theories. In fact, SrVO$_3$ is arguably the simplest correlated metal. It is a simple cubic perovskite, with nominally one electron per V site, which occupies a 3 fold degenerate $t_{2g}$ conduction band. While the presence of a satellite in the photoemission spectra of Ni metal was already well known, in the context of correlated TMOs, the Hubbard band was originally reported in a systematic investigation of Ca$_{1-x}$Sr$_x$VO$_3$ [6], which was followed by many subsequent studies, including ARPES [7,9] and comparison with theoretical predictions (see for instance Refs. [10,11] among others).

One of the most salient features in SrVO$_3$ is the observation of a broad peak at an energy of about $-1.5$ eV in angle integrated photoemission spectra, (upper black curve in Fig. 1), which is interpreted as a Hubbard satellite linked to the V $t_{2g}$ electrons. This feature is also seen in a large range of $3d^1$ materials [20,21]. The ratio of spectral strength between the quasiparticle state and the incoherent satellite in SrVO$_3$ is an important indicator of the magnitude of electron correlations [1,2].
However, photoemission experiments using different photon energies or light brilliance have reported very dissimilar values for such ratio \[11\], making the quantitative benchmarking of realistic \textit{ab-initio} theories for correlated-electron systems difficult \[6, 11, 17, 22, 23\]. Moreover, as shown in Fig. 1 a broad peak at about the same energy is also observed in several \(d^0\) TMO cubic perovskites, such as SrTiO\(_3\), KTaO\(_3\), or anatase TiO\(_2\). Nevertheless, in all these cases the feature has been clearly linked to the presence of oxygen defects \[24–31\]. Interestingly, recent \textit{ab initio} calculations show that spectral weight at \(-1.3\) eV in SrTiO\(_3\) most likely is not of Ti \(t_{2g}\) orbital character, but should be understood as an in-gap defect state with Ti \(e_g\) character \[32–35\]. Thus, we are confronted with the fact that at about 1.5 eV below the Fermi level, we find the lower Hubbard bands of \(d^1\) systems as well as the in-gap states of oxygen-deficient \(d^0\) systems. In view of these observations one may unavoidably wonder (and worry), despite the great success of DMFT methods, whether the putative Hubbard satellite of SrVO\(_3\) might also originate from oxygen vacancies states. Moreover, one should also worry about the possibility of these extrinsic states affecting the features of the conduction band dispersion.

In the present work we resolve these issues in a thorough manner. We present a systematic photoemission study of SrVO\(_3\), to demonstrate dramatic consequences in the spectra due to production of oxygen vacancies.

Using ARPES, we directly show that the UV/X rays used for measurements can produce a large enhancement, of almost an order of magnitude, of the peak at \(-1.5\) eV, similar to the effect observed in \(d^0\) oxide insulators \[24, 27, 30\]. Despite these significant effects on the energy states around the Mott-Hubbard band, we...
are able to determine the intrinsic bulk SrVO$_3$ photoemission spectrum. We find that when the presence of oxygen vacancies is avoided, a clear signal of the correlated Hubbard band remains. We support the interpretation of the experimental data by means of state-of-the-art LDA+DMFT calculations on SrVO$_3$ with oxygen vacancies. Consistent with our experimental data, the calculations show that oxygen vacancies produce states (of $e_g$ symmetry) at energies near the Hubbard satellite. While our study provides definite evidence of a correlated Hubbard band in SrVO$_3$ as predicted by DMFT, it also underlines the significant effects due to oxygen vacancies, which may also affect photoemission data in other TMOs.

Figure 2(a) shows the integrated photoemission spectra of SrVO$_3$ as a function of the UV dose, measured at the CASSIOPEE beamline of SOLEIL Synchrotron under the same conditions of UV light brilliance (about $\sim 5 \times 10^6$ photons s$^{-1}$µm$^{-2}$) of any standard ARPES experiment at a third-generation synchrotron. The measurements were done by continuously irradiating the sample with $h\nu = 33$ eV photons while recording the spectra as a function of irradiation time, with an accumulation time of about 2 minutes per spectrum. The blue and black curves show spectra for the lowest and highest measured doses, obtained respectively after $\sim 2$ minutes and $\sim 2$ hours of irradiation. These data clearly demonstrate that the very UV/X rays used for photoemission experiments can effect radical changes in the measured spectra of SrVO$_3$. Note in fact that a similar effect has been observed for VO$_2$ [37]. In particular, from Fig. 2(a) we observe that the amplitude of the in-gap state at $-1.5$ eV, and more significantly, the ratio of in-gap to quasiparticle (QP) amplitudes, strongly increase with increasing UV dose, going from about 1 : 3 in a pristine sample to more than 2 : 1 in a heavily irradiated sample. Importantly, note that the QP peak position remains basically dose-independent, implying that the carriers created by the UV/X irradiation do not significantly dope the conduction band, and form dominantly localized states. This is confirmed in Fig. 2(b), which shows that the Fermi momenta of the QP band, given by the peaks’ positions in the momentum distribution curves (MDCs) at $E_F$, are also dose-independent. Additional data presented in the Supplemental Material further demonstrate that our measurements yield the expected 3D bulk Fermi surface of SrVO$_3$. Thus, the observed increase in intensity of the in-gap state upon UV irradiation cannot be ascribed to a change in filling of the conduction band, which could have affected the electron correlations. Instead, this unambiguously shows the light-assisted formation of localized defect states at essentially the same energy as that of the expected intrinsic lower Hubbard band—which should then resemble the in-gap peak observed at the lowest UV doses.

In fact, as mentioned previously, it is well established that strong doses of UV/X rays create a large concentration of oxygen vacancies in several $d^9$ perovskites [24-31,33-39]. As illustrated in Figs. 2(c, d) for the case of SrTiO$_3$, the progressive doping of the surface region with oxygen vacancies, due to synchrotron UV irradiation, has two effects: formation of a very intense in-gap state at about $-1.3$ eV, and, in contrast to SrVO$_3$, simultaneous creation of a sharp QP peak at $E_F$ corresponding to a confined quasi-2D electron gas (2DEG) at the samples’ surface. The effective mass of such 2DEG, precisely determined by ARPES, matches the mass expected from density functional theory calculations [24, 25, 39, 40]. Thus, as in SrVO$_3$, the increase in intensity of the in-gap state observed in SrTiO$_3$ upon UV/X irradiation cannot be due to an onset or increase of electron correlations, and should be ascribed to an extrinsic effect.

We therefore conclude that, in SrVO$_3$, exposure to synchrotron UV/X rays creates oxygen vacancies, which are in turn responsible for the extrinsic increase in intensity of the in-gap state evidenced by our measurements. This effect, never discussed or taken into account before, can seriously obscure the determination of the intrinsic spectral function of this model system, thus hampering the advancement of valid theories for correlated-electron systems.

All the previous findings imply that the correct experimental determination of the intrinsic spectral function of SrVO$_3$ should (i) use samples that from the beginning have the lowest possible concentration of oxygen vacancies, and (ii) use doses of UV or X-ray light low enough to avoid any change in the measured spectra. To this end, we measured bulk crystalline thin-films of SrVO$_3$/Nb:SrTiO$_3$ grown in-situ, in a pulsed laser deposition (PLD) chamber directly connected to the ARPES setup, at the beamline 2A of KEK-Photon Factory (KEK-PF) [9,11]. The PLD growth was performed under a pressure below $10^{-7}$ Torr, to obtain an UHV-clean surface, using a Sr$_2$O$_7$ target, which has excess oxygen with respect to SrVO$_3$, thus minimizing the formation of vacancies during the growth—see the Supplemental Material for further details. Furthermore, the UV light brilliance used in these experiments was about 100 times lower than the one in Figs. 2(a, b) from measurements at SOLEIL. We checked (Supplemental Material) that under these conditions the spectra did not change with time, even after several hours of measurements. The resulting energy-momentum ARPES map is presented in Fig. 2(e). One clearly observes the dispersion in the QP band along with the weaker intensity in-gap state, the intrinsic lower Hubbard band, similar as previously reported [7]. By contrast, Fig. 2(f) shows the momentum-resolved electronic structure of a sample, measured at SOLEIL, that was intensively irradiated. There, the peak at $-1.5$ eV becomes broader, more intense, and non-dispersive—all characteristic signatures of a high random concentration of oxygen vacancies.

To rationalize from a microscopic point of view the
Influence of oxygen vacancies on the electronic structure of SrVO₃, we performed charge self-consistent LDA+DMFT calculations for bulk SrVO₃ and various relaxed oxygen-deficient SrVO₃ supercells. The latter are computationally demanding calculations. We shall focus here on the case of a 2 × 2 × 3 supercell with two oxygen vacancies located at opposite apical sites of one vanadium atom, as shown in the inset of Fig. 3(b). We use such vacancy arrangement as it is the prototypical one for d⁹ compounds [39].

For our LDA+DMFT calculations we chose values of U = 2.5 eV and J = 0.6 eV for vanadium and included the effects of bandwidth renormalization due to dynamically screened Coulomb interactions by following the prescription suggested in Ref. [42] (the LDA+DMFT unrenormalized data are shown in the Supplemental Material). In Figs. 3(a) and (c) we show, respectively, the results of the k-integrated and k-resolved spectral functions for bulk SrVO₃ without oxygen vacancies. We find the expected features of a t₂g quasiparticle peak at the Fermi level and a lower Hubbard band at negative energies of the same t₂g nature, in agreement with the photoemission spectra in Figs. 2(a) and (e). The light band at E_F along k<100>, Fig. 2(c), consists of two degenerate bands of dₓᵧ and dₓz characters, while the heavy band along the same direction has dᵧz character. While comparing with the measured k-resolved spectral function, Fig. 2(e), one should bear in mind that along Γ-X (or Γ-Y) the heavy dᵧz (or dₓz) bands are silenced by dipole-transition selection rules in the experiment [24]. Inclusion of bandwidth renormalization [42] renders the lower Hubbard band at an energy (−1.6 eV) in reasonable agreement with experiment (−1.5 eV). We adopted values for U and J from the literature, and did not try to optimize the quantitative agreement with the experimental data. As we show below, in the calculations with oxygen vacancies the value used for U facilitates the visualization of the contributions from the Hubbard and localized states to the incoherent peak at ∼−1.5 eV.

The removal of oxygen atoms in the system leads to the donation of two electrons per oxygen to its surrounding. Already at the level of density functional theory (DFT) in the local density approximation (LDA) (see Supplemental Material), we find that most of the charge coming from the additional electrons is transferred to the 3dₓz orbitals of the neighboring V atom, developing into a sharp peak of e_g symmetry located around −1.1 eV, i.e., at an energy close to the position of the experimentally observed oxygen vacancy states. In analogy to the experimental average over many lattice sites, note that averaging among various supercells with different oxygen vacancy locations and concentrations (what is beyond the scope of the present work) would result in a wider in-gap e_g band, as demonstrated for the case of SrTiO₃—see Fig. 3 of Ref. [33]. By including electronic correlations within (bandwidth renormalized) LDA+DMFT we then see that all the experimental observations qualitatively emerge. In fact, the conducting t₂g orbitals develop a lower Hubbard band peaked at energies about −1.8 eV (Fig. 3(b) and (d)) similar to the bulk case without oxygen vacancies. Most notably, this lower Hubbard satellite does not increase in amplitude with the introduction of vacancies, but rather broadens. In addition, the oxygen-vacancy defect states situated at about −1 eV remain qualitatively unchanged by the correlation effects, but experience a broadening with respect to the pure LDA case. This is in agreement with the photoemission data, evidencing that the increase in intensity of the in-gap state in the oxygen-deficient SrVO₃ is not to be attributed to an increase in population of the lower Hubbard satellite, but instead to the manifestation of vacancy states of e_g character.

In summary, we performed a detailed study of the effects of oxygen vacancies in the spectroscopy of the archetypal strongly correlated electron system SrVO₃. We found that oxygen vacancy states, which are created by UV/X-ray irradiation, occur at energies close to the Hubbard satellite. This dramatically affects the measured line-shape of the Mott-Hubbard band and the ratio of intensities between the quasi-particle and the Mott-Hubbard peaks. By means of a systematic study
under controlled irradiation dose and avoiding the formation of oxygen vacancies, we were able to obtain the intrinsic occupied spectral function of the bulk SrVO$_3$ system. Our experimental interpretation is supported by LDA+DMFT calculations, which provided further insight on the likely nature of the oxygen vacancy states.

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SUPPLEMENTAL MATERIAL

Experimental Methods

Sample preparation

The SrVO$_3$ thin films measured at SOLEIL were grown at the GEMaC laboratory, onto atomically flat TiO$_2$-terminated (100) SrTiO$_3$ substrates by pulsed laser deposition (PLD) under a partial oxygen pressure of 5 × 10$^{-6}$ Torr at temperature of 750°C. A 248 nm wavelength KrF excimer laser was employed with a repetition rate of 1 Hz and a fluency of 1.9 J/cm$^2$. During the growth, surface structure was characterized by Reflection High-Energy Electron Diffraction (RHEED). After the growth, oxygen pressure was reduced to 5 × 10$^{-8}$ Torr when the sample was cooled to room temperature. Surface morphology was carried out with atomic force microscopy (AFM, Bruker Dimension 3100) in tapping mode and the Root Mean Square (rms) roughness of the film was 0.4 nm. To clean the surfaces in UHV prior to ARPES experiments at SOLEIL, the SrVO$_3$ thin films were annealed at a temperature $T = 550$ °C for $t = 5 – 20$ min at pressures lower than $p < 2 × 10^{-8}$ Torr. One of the samples was Ar$^+$ sputtered ($U = 1000$ V, $t = 7$ min) prior to the UHV annealing, without noticeable changes in the ARPES data. After the UHV annealing, the quality of the surfaces was confirmed by low-energy electron diffraction (LEED).

The SrVO$_3$ films measured at KEK were grown in-situ, on a PLD chamber directly accessible from the ARPES UHV chamber, on single-crystalline 0.05 wt% Nb-doped SrTiO$_3$ (001) substrates. The substrates were annealed at 1050°C under an oxygen pressure of $\sim 8 \times 10^{-8}$ Torr to obtain atomically flat TiO$_2$-terminated surfaces. The SrVO$_3$ thin film was deposited on the substrate at 850°C, under a high vacuum below $\sim 10^{-7}$ Torr, to obtain an UHV clean surface, using a Sr$_2$V$_2$O$_7$ target, which has excess oxygen with respect to SrVO$_3$, and thus minimizes the formation of vacancies during the growth. LEED measurements confirmed clean crystalline SrVO$_3$ films with a c(4 × 4) surface reconstruction. The surface morphology of the measured thin films was confirmed by ex-situ atomic force microscopy, showing atomically flat step-and-terrace structure. The coherent growth of these SrVO$_3$ thin film was confirmed by four-circle X-ray diffraction measurements. The characterization results are essentially identical to those reported in previous studies [41, 43, 44], and indicate that there are no detectable structural disorders in the prepared SrVO$_3$ thin films grown on Nb:SrTiO$_3$ (001) substrates.

ARPES measurements

The ARPES measurements were conducted at the CASSIOPEE beamline of Synchrotron SOLEIL (France), and at beamline 2A of KEK-Photon Factory (KEK-PF, Japan). We used linearly polarized photons in the energy range 30 – 110 eV and hemispherical electron analyzers with vertical slits at SOLEIL and horizontal slits at KEK-PF. The angular and energy resolutions were 0.25° and 15 meV. The mean diameter of the incident photon beam was smaller than 100 μm. The UV light brilliance, measured using calibrated photodiodes, was $\approx 5 \times 10^9$ photons s$^{-1}$μm$^{-2}$ at SOLEIL, and about 100 times smaller at KEK-PF. The (001) oriented SrVO$_3$ samples were cooled down to $T = 20$ K before measuring. Unless specified otherwise, all data was taken at that temperature. Measuring at such low temperature minimizes any possible diffusion of oxygen vacancies into the bulk. The results have been reproduced on more than 5 samples. All through this paper, directions and planes are defined in the cubic unit cell of SrVO$_3$. We note [hkl] the crystallographic directions in real space, ⟨hkl⟩ the corresponding directions in reciprocal space, and ⟨hk⟩ the planes orthogonal to those directions. The indices $h$, $k$, and $l$ of Γ$_{hk}$ correspond to the reciprocal lattice vectors of the cubic unit cell of SrVO$_3$.

Surface umklapp bands in thin-films of SrVO$_3$

The surface reconstruction in our SrVO$_3$ thin films leads to the occurrence of surface umklapp bands in the ARPES spectra, as shown in Figs. 4(a, b) for data taken with linear horizontal and linear vertical photons polarizations, respectively. These extra bands, best observed with linear horizontal photons, result simply from the folding of the bulk bands at the surface due to the super-
position of the bulk and the reconstructed surface periodicities. Their presence is a final-state effect and does not affect the bulk electronic structure or the effects due to oxygen vacancies discussed in this work. Note that the spectra taken with linear vertical photons show both the light and heavy bands expected for the intrinsic bulk electronic structure of SrVO$_3$, discussed in the next section.

### Bulk electronic structure of SrVO$_3$

Figure 5 presents a zoom around $\Gamma$ of the ARPES energy-momentum map shown in Fig. 4(b), which was taken using linear vertical photons and a hemispherical electron analyzer with horizontal slits. This configuration of experimental geometry and light polarization allows observing both the light and heavy conduction bands of SrVO$_3$. We fit these bands using simple cosine dispersions of the form $E(k) = E_0 - 2t \cos(ka)$, where $E_0$ is a constant, $4t$ is the bandwidth, and $a$ is the in-plane lattice parameter of the SrVO$_3$ thin films ($a = 3.905$ Å in the case of films grown on SrTiO$_3$). For small $ka$, each cosine band can be approximated by a free-electron-like parabola of effective mass $m^*$ given by $ta^2 = \hbar^2/(2m^*)$. The best fits, shown by the continuous red curves in Fig. 5, yield effective masses $m^*_l = 0.9m_e$ and $m^*_h = 5.5m_e$ for the light and heavy bands, respectively ($m_e$ is the free electron mass).

Figures 6(a, b) show the ARPES Fermi surface maps of SrVO$_3$ cut, respectively, along the $k_x - k_y$ and $k_y - k_z$ planes (or in-plane and out-of-plane). As was shown in Figs. 2(a, b), the Fermi momenta and band filling of the QP conduction band are independent of the UV dose. This ensures that the Fermi surface maps are exempt of extrinsic spurious effects due to the UV-assisted creation of oxygen vacancies.

Our measured Fermi surface agrees with previous ARPES reports on the electronic structure of SrVO$_3$ [7–9]. Furthermore, the bulk 3D character of our measured Fermi surface is demonstrated by the observation, in Fig. 6(b), of dispersive $d_{yz}$ states forming a quasi-circular Fermi sheet in the $k_y - k_z$ plane (green dashed circle serving as guide to the eye).

The 3D density of carriers in the bulk conduction band ($n_{3D}$) can be directly calculated from the volume enclosed by the measured Fermi surface ($V_F$) as $n_{3D} = V_F/4\pi^3$. In very good approximation, $V_F$ corresponds to the volume of three mutually orthogonal inter-penetrating cylinders of cross-sectional Fermi radius $k_F = 0.4$ Å$^{-1}$ and length $2\pi/a$ ($a$ is the cubic lattice constant of SrVO$_3$), i.e.: $V_F \approx 3 \times \pi k_F^2 \times 2\pi/a - 2 \times (4/3)\pi k_F^3$, where the last term avoids counting three times the inner Fermi quasi-sphere at the intersection of the three cylinders. This gives $n_{3D} \approx 0.9e^-/a^3$ ($a^3$ is the unit-cell volume), which is in excellent agreement with the expected value of 1 electron per Vanadium. This again confirms that our ARPES measurements probe the 3D bulk Fermi surface.

FIG. 4. Energy-momentum ARPES intensity maps spanning 3 consecutive Brillouin zones on an SrVO$_3$ thin film prepared in-situ. Vertical dashed red lines show the edges of the bulk unreconstructed Brillouin-zone. The data were measured at KEK-PF using $h\nu = 88$ eV photons with (a) linear horizontal and (b) linear vertical polarizations, and a hemispherical electron analyzer with horizontal slits. The sample temperature was 20 K. Surface umklapp bands induced by the surface reconstruction are best observed in the data using linear horizontal polarization. The spectra taken with linear vertical photons reveal the light and heavy bands of the intrinsic bulk electronic structure of SrVO$_3$. 

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FIG. 5. Zoom around $\Gamma$ of the energy-momentum ARPES intensity map shown in Fig. 4(b), measured at KEK-PF using $h\nu = 88$ eV photons with linear vertical polarization and a hemispherical electron analyzer with horizontal slits. Vertical dashed red lines show the Brillouin-zone edges. Continuous red curves are cosine fits to the bands.

### Electronic structure of vacancy-free SrVO$_3$ using ultra-low dose UV light

Fig. 7 shows photoemission integrated spectra of a bulk SrVO$_3$/SrTiO$_3$ thin-film prepared and measured in-situ at KEK-PF. This eliminates the need to re-anneal in vacuum to clean the surface, and thus minimizes the formation of oxygen vacancies before the measurements. Additionally, the spectra were measured using ultra-low doses of UV light. As can be seen from the figure, this careful measurement protocol prevents the formation of oxygen vacancies, allowing to acquire high-quality data that shows no significant evolution with accumulation time, even after several hours of measurements. Thus, we define the obtained spectra as the “intrinsic” (occupied part of the) spectral function of SrVO$_3$. Hence, the intrinsic ratio between the intensities of the lower Hubbard band and the QP peak is $1:3$.

### Raw ARPES data: vacancy-free vs vacancy-full SrVO$_3$

Figs. 8(a, b) show the raw ARPES data for the QP and lower Hubbard band dispersions in a vacancy-free sample measured under low UV dose, corresponding to the second derivative of Fig. 2(f).

As mentioned in the main text, in the vacancy-free sample the QP band and intrinsic lower Hubbard band show the same dispersion, while in the sample that has been strongly irradiated, and has thus a large concentration of oxygen vacancies, the peak at $-1.5$ eV becomes broader, more intense, and non-dispersive.

### Theoretical Methods

**LDA and LDA+DMFT Calculations**

For the DFT in the local density approximation (LDA) and LDA+DMFT calculations we consider a $2 \times 2 \times 3$ supercell where two adjacent oxygen atoms to a vanadium have been removed. This leads to a stripe-like configuration of vacancies with a concentration of $2/36 \approx 5.56\%$. The internal atomic positions of this structure has been relaxed using the GPAW code [45].

For the LDA+DMFT calculations (see Ref. [46] for a detailed explanation) we used the WIEN2k [47] implementation in the local density approximation in combination with a continuous-time quantum Monte Carlo (CTQMC) impurity solver in the hybridization expansion [48] from the ALPS [49, 50] project. We projected the Bloch wave functions onto localized V $3d$ orbitals [14, 51] in the unit cell, leading to a set of 6 inequivalent impurities for the two vacancy structure. Within the DMFT approximation we assume that (i) the multiple impurity atoms only hybridize with an effective bath that is determined self-consistently and (ii) the intersite hybridization to be small. This allows us to solve the impurity problems separately and to write the full self-energy in Bloch space as

$$\Sigma_{\nu \nu'}(k, i\omega_n) = \left( \sum_a P^\dagger_a(k) \Sigma^a(i\omega_n) P_a(k) \right)_{\nu \nu'},$$

where the sum is performed over all impurity atoms $a$, with the corresponding projection operators $P_a(k)$. The projection comprises the V $t_{2g}$ and $e_g$ orbitals in the energy window $[-1.5, 6.0]$ eV. The calculations were performed for the inverse temperature $\beta = 40$ eV$^{-1}$ (290 K) with the interaction parameters used in the definition of the Slater integrals [52] with average $U = 2.5$ eV and $J_H = 0.6$ eV. For the double counting correction we used the FLL [53, 54] scheme and we checked that different values of the double counting only lead to small quantitative changes in the spectral function. The continuation of the Monte Carlo data to the real axis was done by stochastic analytic continuation [55].
(a) In-plane Fermi-surface of SrVO$_3$(001), measured using linear horizontal photons at $h\nu = 72$ eV, and a hemispherical electron analyzer with vertical slits. (b) Out-of-plane Fermi surface of SrVO$_3$(001), measured using linear vertical photons from 30 eV to 95 eV, in steps of 1 eV, and a hemispherical electron analyzer with vertical slits. The green dashed circle is as guide to the eye showing the quasi-circular Fermi-surface formed by the $d_{yz}$ states. In both panels, the red lines delimit the Brillouin-zone. All data from this figure were measured at CASSIOPEE (SOLEIL), using the same light brilliance conditions of Figs. 2(a, b).

FIG. 7. Photoemission spectra of SrVO$_3$ as a function of irradiation time using an ultra-low dose of UV light. The sample was prepared in-situ. This eliminates the need to re-announce in vacuum to clean the surface prior to measurements, and thus minimizes the formation of oxygen vacancies. The energy distribution curves (EDCs) were extracted from ARPES data around the $\Gamma$$_{003}$ point integrated along the $k$ =< 100 > direction. The blue and black curves show spectra for the lowest and highest measured doses, obtained respectively after $\sim$ 2 minutes and $\sim$ 2 hours of irradiation. The data from this figure were measured at KEK-PF using $h\nu$ = 88 eV photons with linear horizontal polarization, and a hemispherical electron analyzer with horizontal slits.

Standard LDA+DMFT vs. LDA+DMFT including dynamical screening

In this work we included the effects of bandwidth renormalization due to dynamically screened Coulomb interactions using a low-energy effective model with an effective Hamiltonian

$$H_{\text{eff}} = - \sum_{i,j,\sigma} Z_B t_{ij} d_i^{\dagger} d_j + U_0 \sum_i d_i^{\dagger} d_i^{\dagger} d_i d_i,$$

with the screened Hubbard interaction $U_0$. This approach has been suggested in Ref. [42], and proved to be a good approximation to the full treatment of the dynamically screened Coulomb interaction. For the bandwidth renormalization factor we used $Z_B = 0.7$ [42].

In Fig. 9 we show a comparison between standard DFT, “standard” LDA+DMFT and the LDA+DMFT approach including the effective screening of the Coulomb interaction for a)-c) bulk SrVO$_3$ and d)-f) the two vacancy structure of SrVO$_3$. The main effect of including the Coulomb interaction screening via this approach is a shift of the upper and lower $t_{2g}$ Hubbard bands towards the Fermi level, originating from the effective reduction of bandwidth. Compared to experiment (as discussed in the main text), “standard” LDA+DMFT consistently locates the lower Hubbard band at higher binding energies, in both the bulk and vacancy structure, whereas the effective model yields a much better agreement. Especially in the bulk system the position of the lower Hubbard band...
is brought to a good agreement.

Finally, the calculations with oxygen vacancies produce a ladder of heavy bands near $E_F$, that originate from the non-equivalency in all the vanadium atoms of the super-cell contributing $t_{2g}$ bands near the Fermi level. This V non-equivalency is due to the presence of oxygen vacancies that lower the symmetry. In the more realistic case with larger cells, only the in-gap $e_g$ states of the V near the vacancy/vacancies would produce a significant spectral feature, while essentially all the V atoms of the cell would be equivalent, and the effects of the $t_{2g}$ states coming from the few non-equivalent vanadium atoms around the vacancy would be negligible. At present, such a calculation is however computationally unfeasible in the framework of LDA+DMFT.

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FIG. 9. (Color online) Comparison for bulk SrVO₃ between (a) the DFT result, (b) the LDA+DMFT result, and (c) the LDA+DMFT including an effective treatment of the dynamical Coulomb interaction screening (explained in the main text) indicated by a *. (d-f): Same comparison for the 2 vacancy structure of SrVO₃. The main effect of the renormalization factor is a shift of the upper and lower t₂g Hubbard bands towards the Fermi level, yielding a better agreement with experiment.

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