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

S. Backes,$^1$ T. C. Rödel,$^{2,3}$ F. Fortuna,$^2$ E. Frantzeskakis,$^2$ P. Le Fèvre,$^3$ F. Bertran,$^3$ M. Kobayashi,$^4$ R. Yukawa,$^4$ T. Mitsuhashi,$^4$ M. Kitamura,$^4$ K. Horiba,$^4$ H. Kumigashira,$^4$ R. Saint-Martin,$^1$ A. Fouchet,$^6$ B. Berini,$^6$ Y. Dumont,$^6$ A. J. Kim,$^1$ F. Lechermann,$^1,8$ H. O. Jeschke,$^1$ M. J. Rozenberg,$^9$ R. Valentí,$^1,*$ and A. F. Santander-Syro$^2,1$

$^1$Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, 60438 Frankfurt am Main, Germany
$^2$CSNSM, Univ. Paris-Sud, CNRS/IN2P3, Université Paris-Saclay, 91405 Orsay Cedex, France
$^3$Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin BP48, 91192 Gif-sur-Yvette, France
$^4$Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba 305-0801, Japan
$^5$SP2M-ICMMO - UMR-CNRS 8182 Université Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France
$^6$GEMaC, Université de Versailles St. Quentin en Y. - CNRS, Université Paris-Saclay, Versailles, France
$^7$Institut für Theoretische Physik, Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany
$^8$Institut für Keramische Hochleistungswerkstoffe, TU Hamburg-Harburg, D-21073 Hamburg, Germany
$^9$Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France

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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 spectroscopy (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 ARPES spectrum in the limit of a negligible concentration of vacancies, where a clear signal of a lower Hubbard band remains. We support our study by means of state-of-the-art $ab\text{ initio}$ 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 with the ubiquitous oxygen vacancies as extensively reported in the context of a two-dimensional electron gas at the surface of insulating $d^0$ transition metal oxides.

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Introduction. 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 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 $ab\text{ initio}$ density functional methods [local density approximation (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 separates from 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 threefold 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 angle-resolved photoemission spectroscopy (ARPES) [7–9] and comparisons with theoretical predictions (see, for instance, Refs. [10–20], 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 $t_{2g}$ electrons. This feature is also seen in a large range of $3d^1$ materials [21,22]. The ratio of spectral strength between the quasiparticle (QP) 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 a ratio [11], making the quantitative benchmarking of realistic $ab\text{ initio}$ theories for correlated electron systems difficult [6,11,18,23,24]. 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 [25–32]. Interestingly, recent ab initio calculations show that the 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 [33–36]. Thus, we are confronted with the fact that at about 1.5 eV below the Fermi level ($E_F$), 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 vacancy states. Moreover, one should also worry about the possibility of these extrinsic states affecting the features of the conduction band dispersion.

In the present Rapid Communication 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 the creation of oxygen vacancies. Using ARPES, we directly show that the UV or x-rays used for photoemission experiments cannot produce 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 [25–28,37]. Despite these significant effects on the energy states around the Mott-Hubbard band, we are able to determine the full SrVO$_3$ photoemission spectrum in the limit of a negligible concentration of vacancies, where a clear signal of the dispersive 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 definitive 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.

**Methods.** The bulk-like relaxed, crystalline (001) oriented SrVO$_3$ thin films were grown by pulsed laser deposition (PLD) either at the GEMaC laboratory, then measured at the CASSIOPEE beamline of Synchrotron SOLEIL, or in a PLD chamber directly connected to the ARPES setup at beamline 2A of KEK-Photon Factory (KEK-PF) [9,38,39]. To clean the surfaces in UHV prior to ARPES experiments at SOLEIL, the SrVO$_3$ thin films were annealed at 550°C for $t=5$–20 min at pressures lower than $2 \times 10^{-5}$ Torr. At KEK-PF, the PLD growth was performed under a pressure below $10^{-7}$ Torr, to obtain UHV-clean surfaces, using a Sr$_2$V$_2$O$_7$ target, which has excess oxygen with respect to SrVO$_3$, thus minimizing the formation of vacancies during the growth. In all cases, the surface quality was confirmed right before ARPES measurements by low-energy electron diffraction (LEED). The thin films measured at KEK-PF showed a $(4 \times 4)$ surface reconstruction, which does not affect the analysis and conclusions of this work. For the ARPES measurements 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 samples were cooled down to $T=20$ K before measuring. Unless specified otherwise, all data were taken at that temperature. The results were reproduced on more than five samples. All through this Rapid Communication, directions and planes are defined in the cubic unit cell of SrVO$_3$. We denote [hkl] the crystallographic directions in real space, (hkl) the corresponding directions in reciprocal space, and (hkl) the planes orthogonal to those directions. The indices $h$, $k$, and $l$ of $\Gamma_{hkl}$ correspond to the reciprocal lattice vectors of the cubic unit cell of SrVO$_3$. The Supplemental Material [40] presents further details about the sample growth and measurements.

**Experimental results.** Figure 2(a) shows the integrated photoemission spectra of SrVO$_3$ as a function of the UV dose, measured at CASSIOPEE SOLEIL under the same conditions of light brilliance of any standard ARPES experiment at a third-generation synchrotron. The measurements were done by continuously irradiating the sample with $hv=33$ eV photons while recording the spectra as a function of irradiation time, with an accumulation time of about 2 min per spectrum. The blue and black curves show spectra for the lowest and highest measured doses, obtained respectively after $\sim 2$ min and $\sim 2$ h of irradiation. These data clearly demonstrate that the very UV or x-rays used for photoemission experiments can produce radical changes in the measured spectra of SrVO$_3$. Note in fact that a similar effect has been observed for VO$_2$ [41]. In particular, from Fig. 2(a) we observe that the amplitude of
FIG. 2. (a) Photoemission spectra of SrVO$_3$ as a function of UV dose, measured at Synchrotron SOLEIL ($h\nu = 33$ eV). The energy distribution curves (EDCs) were extracted from raw ARPES data around the $\Gamma_{002}$ point integrated along the $k = \langle 010 \rangle$ direction. 
(b) Corresponding momentum distribution curves (MDCs) integrated over 50 meV below $E_F$. Peaks in the MDCs indicate the Fermi momenta.
(c), (d) Same as (a), (b) for SrTiO$_3$ ($h\nu = 47$ eV). The filling of a 2DEG upon UV irradiation is evidenced by the formation of QP peaks in the EDCs and MDCs at $E_F$ [inset of (c) and (d), respectively]. All data were taken at 20 K.

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 or 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 peak 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 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 or 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 can seriously obscure the determination of the spectral function of this model system, thus hampering the advancement of valid theories for correlated electron systems.

The findings described above imply that the correct experimental determination of the vacancy-free photoemission spectrum 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 light-induced changes in the measured spectra. To this end, we measured SrVO$_3$ thin films grown directly in situ at beamline 2A of KEK-PF. As mentioned before, the growth protocol of such thin films minimizes the formation of vacancies, while the UV light brilliance at KEK-PF is $\sim 100$ times smaller than the one in Figs. 2(a) and 2(b) from measurements at SOLEIL. We checked (see the 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, and its second derivative, are presented in Figs. 3(a) and 3(b). One clearly observes the dispersing QP band along with a also dispersive in-gap state of weaker intensity, corresponding to the intrinsic spectral function of SrVO$_3$ will then be given by such a photoemission spectrum, which approaches the vacancy-free limit, modulo dipole-transition matrix elements, inherent to
FIG. 3. (a) Energy-momentum ARPES intensity map measured at KEK-PF with a low UV dose on a SrVO₃ sample prepared in situ, using a well-established protocol to minimize the formation of oxygen vacancies (see the main text and Supplemental Material). Note that due to the choice of light polarization, the heavy bands along (100) are not observed and only the contribution of the light dₓᵧ band is detected. The data were acquired at hν = 88 eV around Γ₁₀₃. (b) Second derivative (negative values) of the map in (a). The use of second derivatives allows a better visualization of the dispersion of both the quasiparticle and Mott-Hubbard bands on the same color plot. The dispersionless feature at Eₘ₎ is a spurious effect of such a second derivative on the Fermi-Dirac cutoff. (c), (d) Same as (a), (b) after a strong UV irradiation dose, measured at SOLEIL (hν = 33 eV), typical of modern third-generation synchrotrons. The measurements were done at hν = 33 eV close to Γ₀₀₂. All data were taken at 20 K. Note that at constant photon energy, ARPES maps out the electronic structure at a spherical surface of three-dimensional (3D) k space, which can be locally approximated to a plane for all our measurements (details in the Supplemental Material). The different choice of photon energies and k-space positions for measurements at KEK-PF [(a) and (b)] and SOLEIL [(c) and (d)] was dictated by the different geometrical configurations and constraints of the beamlines in both synchrotrons.

the photoemission process, which can still modulate the intensity of the QP peak relative to the Hubbard peak. A calculation of such matrix elements requires a full one-step calculation of the photoemission process, which is beyond the scope of this work. By contrast, Figs. 3(c) and 3(d) show 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 nondispersive—all characteristic signatures of a high random concentration of oxygen vacancies.

Numerical calculations. 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. 4(b). We use such a vacancy arrangement as it is the prototypical one for d⁰ compounds [43].

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. [45] (the LDA+DMFT unrenormalized data are shown in the Supplemental Material). In Figs. 4(a) and 4(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 Fig. 2(a) and Figs. 3(a) and 3(b). The light band at Eₘ₎ along k₁₀₀ [Fig. 4(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 [Figs. 3(a) and 3(b)],
we find that most of the charge coming from the local density approximation (LDA) (see the Supplemental Material), we find that most of the charge coming from the local density approximation (LDA) (see the Supplemental Material). By including electronic correlations within (bandwidth renormalized) LDA+DMFT we then see that all the experimental observations qualitatively emerge. In fact, the conducting $t_{2g}$ orbitals develop a lower Hubbard band peaked at energies about $-1.8 \text{ eV}$ [Figs. 4(b) and 4(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 $-1 \text{ eV}$ 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 SrVO$_3$ is not to be attributed to an additional, the oxygen vacancy defect states situated at about $-1 \text{ eV}$ 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 SrVO$_3$ 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.

Conclusions. In summary, we performed a detailed study of the effects of oxygen vacancies in the spectroscopy of the archetypal strongly correlated electron system SrVO$_3$. We found that oxygen vacancy states, which are created by UV or 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 quasiparticle and the Mott-Hubbard peaks. By means of a systematic study under a controlled irradiation dose, using samples directly grown in situ, we were able to obtain the photoemission spectrum of the bulk SrVO$_3$ system in the limit of a negligible concentration of oxygen vacancies. Our experimental interpretation is supported by LDA+DMFT calculations, which provided further insight into the likely nature of the oxygen vacancy states.

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