Electronic localization in CaVO₃ films via bandwidth control

Daniel E. McNally¹, Xingye Lu², Jonathan Pellicciani¹, Sophie Beck², Marcus Dantz³, Muntaser Naamneh¹, Tian Shang¹,³, Marisa Medarde⁶, Christof W. Schneider⁵, Vladimir N. Strocov¹, Ekaterina V. Pomjakushina⁶, Claude Ederer², Milan Radovic¹ and Thorsten Schmitt¹

Understanding and controlling the electronic structure of thin layers of quantum materials is a crucial first step towards designing heterostructures where new phases and phenomena, including the metal-insulator transition (MIT), emerge. Here, we demonstrate control of the MIT via tuning electronic bandwidth and local site environment through selection of the number of atomic layers deposited. We take CaVO₃, a correlated metal in its bulk form that has only a single electron in its V⁴⁺ 3d manifold, as a representative example. We find that thick films and ultrathin films (≤6 unit cells, u.c.) are metallic and insulating, respectively, while a 10 u.c. CaVO₃ film exhibits a clear thermal MIT. Our combined X-ray absorption spectroscopy and resonant inelastic X-ray scattering (RIXS) study reveals that the thickness-induced MIT is triggered by electronic bandwidth reduction and local moment formation from V⁴⁺ ions, that are both a consequence of the thickness confinement. The thermal MIT in our 10 u.c. CaVO₃ film exhibits similar changes in the RIXS response to that of the thickness-induced MIT in terms of reduction of bandwidth and V 3d–O 2p hybridization.

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INTRODUCTION

Deposition methods with unit cell thickness precision enable new approaches to control the degree of electronic localization in quantum materials. For instance, epitaxial strain changes the lattice parameters altering the potential landscape of the electrons, dimensionality tunes the electronic bandwidth and interfacing provides a charge reservoir. Thickness-dependent metal-insulator transitions (MIT) in thin films have been widely reported in recent years in a broad swathe of correlated 3d and 5d transition metal oxides. Understanding and controlling the electronic structure of these quantum materials is a critical first step toward designing heterostructures where new emergent phases and phenomena, including MIT, have been widely predicted. The focus of our interest is to resolve the nature of the thickness-induced MIT, therefore, in this work we consider CaVO₃ as a model system.

Bulk CaVO₃ with a formal valence shell configuration of V3d¹ (V⁴⁺ oxidation state) is a paramagnetic metal with enhanced Sommerfeld-Wilson and Kadowaki-Woods ratios suggesting electronic correlations are important. However, as is often the case for metals, neither moderate doping nor pressure induce insulating or magnetic ground states. In contrast to the bulk, enhanced electron correlation strength and a MIT have recently been reported for CaVO₃ films of 20 unit cells (u.c.) or less. While these discoveries are promising for technological applications such as transparent conductors and MottFETs, a complete understanding of the MIT in CaVO₃ has, until now, remained elusive.

Figure 1 illustrates that electronic bandwidth can control the degree of electronic localization in 3d³ perovskites RXO₃. In the example presented in the top panels, applicable for bulk-like materials, when the orthorhombic distortion is increased the bandwidth decreases by up to 40% and a MIT occurs. However, realising this MIT requires the substitution of both R and X ions making it very difficult to continuously control in practice. In our work presented here, we show that the bandwidth can be continuously controlled by up to 40% in CaVO₃ simply by choosing the number of atomic layers deposited on a SrTiO₃ substrate as summarized in the bottom panels of Fig. 1 and outlined in detail in the rest of this work.

RESULTS

MIT in thin film CaVO₃

Figure 2a presents electrical resistance as a function of temperature for our CaVO₃ and SrVO₃ thin films grown by pulsed laser deposition (PLD) on SrTiO₃ (100) substrates. The film thicknesses and surface ordering were routinely monitored with multiple high-energy electron diffraction (RHEED), see Fig. 1 in S.I. For the thinner films (15 u.c., 10 u.c., 6 u.c., 4 u.c. CaVO₃) a thin 2 nm SrTiO₃ overlayer was deposited to protect against environmental (in air) degradation upon removal from PLD chamber. The thick 50 u.c. films are metallic at all temperatures, like bulk CaVO₃ and SrVO₃, when the CaVO₃ (CVO) film thickness is reduced an MIT occurs. The 15 and 10 u.c. films undergo an MIT at 160 and 220 K, respectively, while the 6 and 4 u.c. films are insulating at all temperatures (the 4 u.c. film was too insulating to be measured using our setup). The overall behaviour is similar to that previously reported for CaVO₃ films. Comparison of RHEED patterns recorded at room temperature...
after deposition of 15 u.c. CVO (metallic at room temperature) and 6 u.c. CVO (insulating at room temperature) films suggests structural transitions (possibly octahedral rotation) to play a role in the thickness-induced MIT (see S.I. Figure 3). We emphasize that this structural reconstruction was only observed for the very thin CaVO₃ film of 6 u.c. thickness that was capped by a 2 nm (5. u.c.) SrTiO₃ over-layer (compare Figs 1 and 3 in S.I.). We ascribe an important role to the SrTiO₃ over-layer in inducing and/or stabilizing this structural reconstruction.

X-ray absorption (XAS) at the V L₂,₃ edges, presented in Fig. 2b, reveals an evolution from broad d-bands and large valence fluctuations in metallic thick films of CaVO₃ to a more localized 3d character in the thinner insulating films. XAS of the thick metallic 50 u.c. film (red line) is similar to that of a CaVO₃ single crystal (brown), as well as a 50 u.c. SrVO₃ film (dashed black). These spectra are not well reproduced by multiplet calculations because of the itinerant character of the 3d electrons. With reduced film thickness the XAS spectra become sharper, the L₃ peak energy is reduced by ~0.5 eV, a shoulder appears on the L₃ peak and a new peak is found in the dip between L₃ and L₂ peaks. These new peaks are commonly observed in insulating VO₂ (V⁴⁺, dashed grey) and V₂O₃ (V³⁻) compounds (dashed magenta). In particular, XAS of the thinner most insulating CaVO₃ films (6 and 4 u.c.) is similar to that reported for Y₁₋ₓCaₓVO₃ (x ≥ 0.6) that contains a mixture of V⁴⁺ and V³⁻ character. The increase in V³⁻ results from charge redistribution in the thinner films and is consistent with a reduced Madelung potential and hence reduced V–O covalency across the MIT. The sharpening of the L₂,₃ peaks across the MIT reflects a reduction in the bandwidth of the upper Hubbard band. XAS of the 10 u.c. film in the high temperature metallic state is presented as a dashed blue curve in Fig. 2b. A broadening of the spectral features is observed with respect to the low temperature insulating state but the overall response is still different from that of the metallic thick 50 u.c. CaVO₃ film. We undertook a series of resonant inelastic X-ray scattering (RIXS) measurements to investigate further the change in the electronic excitations across the thickness-induced and thermal MIT.

Fig. 1  Comparison of bandwidth change with cation substitution in bulk 3d¹ crystals with that realized in thin films of CaVO₃ by reducing film thickness. a, b The crystal structure and electronic bandwidth of different 3d¹ perovskites RXO₃ is presented. For R = Sr and X = V a cubic structure is reported. When R is substituted to R = Ca an orthorhombic distortion occurs changing the electronic bandwidth and local V site symmetry. This results in a more correlated metallic state. When R is substituted to R = La and X substituted to X = Ti to maintain 3d¹ configuration, the distortion is further increased and a metal-insulator transition occurs (MIT). The MIT is accompanied by long range antiferromagnetic order that can be switched to ferromagnetic by substituting R to R = Y. c, d A comparable reduction in bandwidth is found when the MIT in CaVO₃ is controlled by film thickness as described in this manuscript.
Control of electronic bandwidth in CaVO₃

Figure 3 presents RIXS intensity maps of energy transfer versus incident energy at \( T = 20 \text{ K} \) across the V L₃ edge. First, we discuss the energy map for the 50 u.c. SrVO₃ and CaVO₃ films presented in panels a and b. Three fluorescence features,\(^2⁰\) where the energy transfer disperses linearly with incident energy, are evident at higher energy transfers (marked as F1, F2 and F3 in Fig. 3c). These spectral signatures have been observed previously for single crystals.\(^2²\) In CaVO₃, and were assigned to, for decreasing energy transfer, a hybridized V–O band (F3), an inter-band transition involving the lower Hubbard band (F2), and an intra-band transition involving a quasiparticle-like band (F1).\(^2¹\) Furthermore, we observe several new Raman-like modes where the energy transfer is independent of incident energy. We assign the intense Raman-like scattering at higher energy transfers (R2) is assigned to crystal-field excitations. The assignment of fluorescence and Raman peaks is illustrated in a schematic representation of occupied and unoccupied density of states in Fig. 3e.

The RIXS response undergoes a large change as we traverse the thickness-induced MIT in CaVO₃. RIXS maps for insulating 10 and 4 u.c. films are presented in Fig. 3c, d. Our first observation is that the spectral weight in the fluorescence features has decreased relative to the spectral weight in the Raman modes as the film thickness is decreased. This transfer of spectral weight from band to localised excitations is expected as we move from metallic to insulating behaviour. We also observe that the measured peaks become sharper and there is a reduction of the bandwidth of these electronic excitations. The reduced bandwidth of electronic excitations measured across the MIT in our RIXS experiment on CaVO₃ is similar to the reduced bandwidth measured using angle-resolved photoemission (ARPES) across the thickness-induced MIT in thin films of another vanadate, SrVO₃, that was ascribed to a dimensional crossover below 3–4 u.c.\(^³\). In the case of CaVO₃ reported here the crossover occurs at a larger thickness of 10 u.c. suggesting that both strain and dimensionality influence the MIT.

Indeed it has been shown that strain can substantially affect the MIT in other systems, such as NdNiO₃.\(^²³\)

We quantify the reduction in the bandwidth of the electronic excitations by fitting the data and present the corresponding line cuts and fit results in Fig. 4. The thickness-dependence of the low energy Raman-like RIXS peak that we assign to electron-hole pair excitations,\(^²⁰,²²,²⁴\) is presented in Fig. 4a. The elastic line has been subtracted and the corresponding fits are presented in S.I. We extract from our fits the bandwidth and energy scale of the electron-hole pair excitations and present these results in Fig. 4c (bottom). The bandwidth is gradually reduced from 0.73 eV in the SrVO₃ 50 u.c. film to 0.63 eV in the CaVO₃ 50 u.c. film down to 0.38 eV in the insulating 6 and 4 u.c. CaVO₃ films. The peak energy exhibits a large jump from 0.5 eV to 0.3 eV from SrVO₃ 50 u.c. to CaVO₃ 50 u.c. and then is gradually reduced to nearly 0.2 eV in the insulating 6 and 4 u.c. films.

In Figs 4b, c (top) we present line cuts and fit results for the fluorescence features F1 and F2 that are band excitations. We illustrate the origin of the F1 and F2 features in Fig. 3 (bottom) and assign F1 to intra-band excitations involving a quasiparticle-like band and F2 to inter-band excitations involving the lower Hubbard band.\(^²¹\) The separation between these two RIXS peaks is ~1.8 eV, the same energy separation as the low-energy optical conductivity peaks that were also interpreted as originating from intra- and inter-band excitations. Further support for this interpretation is provided by photoemission spectra that reveal a lower Hubbard band at 1.8 eV below the Fermi level.\(^²⁵\) The total bandwidth of our two measured RIXS peaks, determined from the first derivative of the spectra (shown in S.I.), scales with the bandwidth of the V 3d valence band.\(^¹⁹\) Fig. 4c (top) presents the results of this analysis. The total bandwidth displays a sharp drop between the metallic 50 u.c. SrVO₃ film (~4 eV) and the 15 u.c. CaVO₃ film (~3.5 eV) that is on the verge of being insulating (see Fig. 2a). The bandwidth continues to decrease gradually to 3.2 eV in the most insulating 4 u.c. CaVO₃ film. A guide for the eye in Fig. 4b shows the reduction in the separation between intra- and inter-band peaks, consistent with the bandwidth reduction extracted from our derivative analysis. For the 4 u.c. film the relative spectral...
weight in the intra-band peak substantially decreases with respect to the inter-band peak (compared to the 50 u.c. CaVO₃ film) as the spectral weight is transferred away from the valence band maximum. However, there is still weight in the intra-band peak even in the insulating phase indicating metallic puddles are still present even in the insulating phase.²⁶

Local moment formation in CaVO₃ films

There are several Raman-like peaks marked as R2 in Fig. 3 and we present line cuts through this region for different film thicknesses in Fig. 5 (left). In the thick metallic 50 u.c. SrVO₃ film, that is nominally a perfect cubic structure with no octahedral tilting and formal valence band configuration of V 3d¹, we observe a broad peak centred around 1.9 eV, a similar energy scale to the t²g→e₉ excitations found near 1.7 eV in the insulator YVO₃ with a valence electron configuration of V 3d².²⁷ For the 50 u.c. CaVO₃ film, that has a small orthorhombic distortion and octahedral tilting, we find a large broadening and nearly flat distribution of spectral weight. A three peaks structure is measured in the 15 u.c. CaVO₃ film and these peaks continue to sharpen in the insulating 10 u.c., 6 u.c. and 4 u.c. CaVO₃ films (Fig. 5 (left)). There are two possible explanations for this reconstruction: strain-induced changes in bond lengths or the formation of local magnetic moments.²⁷ The effect of epitaxial strain is larger in the thinner films but strain effects are expected to lift the degeneracy of the t²g and e₉ states by only a small amount (~100 meV)¹⁵ compared to the large effect reported here. The additional peaks are therefore a clear signature of local moment formation from V³⁺ ions allowing spin flips from a t²g² high spin S = 1 ground state configuration to configurations involving S = 0 and the e₉ level.²⁷ We already have evidence that V³⁺ ions are present in thinner CaVO₃ films from our XAS as described earlier and thus we can attribute the additional peak near 1 eV to a local spin flipping t²g² S = 0 transition at twice the Hund’s coupling energy 2Jₖ using the notation of ref. ²⁷ The additional peak near 2.6 eV is also captured by several overlapping local excitations on the V³⁺ ion, namely by transitions to t²g¹ e₉ with S = 0 or S = 0,²⁷ the formation of a local moment in insulating ultra-thin CaVO₃ films starting from a bulk-like non-magnetic thin film is a dramatic effect, resulting from a control of electronic bandwidth and charge redistribution.

Fig. 3 Overview of resonant inelastic x-ray scattering (RIXS) measurements across a thickness-induced MIT in vanadate thin films. (top) X-ray absorption total fluorescence yield for samples indicated (a–d). RIXS intensity maps of energy transfer versus incident energy for different film thickness across the thickness-induced MIT. CaVO₃ and SrVO₃ metal films are 50 unit cells thick. Illustrative sketch of the origin of the Raman and fluorescence peaks measured using RIXS. The sketch is drawn on the total density of states (DOS) and partial DOS for V 3d e₉ (red) and V 3d t²g (blue) calculated using density functional theory.
Thermal MIT in 10 u.c. CaVO$_3$ film and the role of V–O hybridization

Now we draw the attention to the MIT which occurs below 220 K in the 10 u.c. CaVO$_3$ film (see Fig. 2a). We present in Fig. 6 the RIXS intensity as a function of energy transfer for the 10 u.c. film in the room temperature metallic phase (at 300 K) and at 20 K, deep in the insulating phase. The change in the RIXS response across the thermal MIT is qualitatively similar to the change for the thickness-induced MIT (see also Fig. 4c): the bandwidth of the electron-hole pair excitation decreases by ca. 15% along with a small softening of the peak position (Fig. 6a), the crystal field levels sharpen (Fig. 6b), and the total bandwidth near the valence band maximum decreases by about 5% (Fig. 6c). In addition, we can quantitatively comment on the relative strength of the high-energy V 3d–O hybridization band shown in Fig. 6d: the intensity of this peak is reduced by 10% in the insulating phase.
We thus propose that a structural and/or epitaxial strain. Strain will induce changes in the V\textsuperscript{3+} contributions for the thermal- and thickness-induced MIT. In the thermal and thickness-induced MIT, with the effects on the bandwidth and reduced V\textsuperscript{3+} contributions comparable to those realized in the 3d\textsuperscript{1} perovskite series SrVO\textsubscript{3}-CVO\textsubscript{3} as observed in e.g. nickelate films.\textsuperscript{23} This proposed is supported by the data presented in Fig. 6b that shows a sharpening of crystal field excitations across the thermal MIT. For the thinner CaVO\textsubscript{3} films, the electron-hole bandwidth (see Figs. 1 and 4c, d) is sharply reduced moving from 10 u.c. to 6 u.c. and 4 u. c. films. Additionally XAS reveals increasing V 3d\textsuperscript{2} contributions (Fig. 2b) and the crystal field excitations become much shaper for the thickness-induced MIT (Fig. 5).

The increased contribution from V\textsuperscript{3+} ions in the thinner films stems from charge redistribution and is connected to a reduced V–O covalence across the MIT. The reduction of the V 3d bandwidth is driven by a structural reconstruction accompanied by octahedral rotation, that is thereby also changing the V–O hybridization, manifested in an abrupt change of the RHEED patterns of the ultra-thin capped films. In this sense the ""electronic localization and bandwidth reduction" as well as the ""increase of V\textsuperscript{3+} contributions"" are a consequence of the thickness confinement. Oxygen vacancies generated during the growth of CVO films might partially contribute to V\textsuperscript{3+} states, but their amount, in principle, should scale with the film thickness. However, 50 u.c. CVO film does not show more V\textsuperscript{3+} signature in the spectra than thinner CVO films suggesting no significant influence of oxygen vacancies on the properties of the studied CVO films.

The combined effects of charge redistribution, confinement, as well as strain are important in the ultrathin CaVO\textsubscript{3} films. Based on the results presented here it is difficult to distinguish which of these effects is the main player driving the thickness-induced MIT. However, we note that the MIT appears to be significantly more complex than the dimensional crossover-driven MIT reported in ultrathin SrVO\textsubscript{3} films using ARPES spectroscopy.\textsuperscript{5}

Our experiments reveal a bandwidth-driven MIT in CaVO\textsubscript{3} films as a function of both thickness and temperature where strain, dimensionality and charge redistribution contribute. A reduced V–O hybridization in the insulating state reveals that the MIT is of Mott-Hubbard type where a d–d gap is opened by a strong Coulomb interaction U between electrons.\textsuperscript{30} The sharp thermal MIT observed in our 10 u.c. CaVO\textsubscript{3} film should stimulate future work on this model system. Our results are promising for the future of the field of correlated electronics showing that while increased disorder can be present in ultra-thin films, it does not inhibit the Mott physics and related spin or charge ordering. However, we want to emphasize the radical changes in electronic structure that can occur in films of reduced dimensionality, and the importance of including these effects in the rational design of new quantum materials.

FIG. 6  Resonant inelastic x-ray scattering across the thermal metal-insulator transition in a 10 u.c. CaVO\textsubscript{3} film. a–d Resonant inelastic X-ray scattering (RIXS) intensity as a function of energy transfer at incident photon energy of 520 eV for a 10 u.c. CaVO\textsubscript{3} at 20 K and 300 K. (inset of a) Same with elastic line subtracted
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ADDITIONAL INFORMATION

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