Multi-orbital effects in optical properties of vanadium sesquioxide

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Abstract
Vanadium sesquioxide, V\textsubscript{2}O\textsubscript{3}, boasts a rich phase diagram whose description necessitates accounting for many-body Coulomb correlations. The spectral properties of this compound have been successfully addressed within dynamical mean field theory to the extent that results of recent angle-resolved photoemission experiments have been correctly predicted. While photoemission spectroscopy probes the occupied part of the one-particle spectrum, optical experiments measure transitions into empty states and thus provide complementary information. In this work, we focus on the optical properties of V\textsubscript{2}O\textsubscript{3} in its paramagnetic phases by employing our recently developed ‘generalized Peierls approach’. We obtain results in overall satisfactory agreement with experiments. Further, we rationalize that the experimentally observed temperature dependence stems from the different coherence scales of the charge carriers involved.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Vanadium sesquioxide, V\textsubscript{2}O\textsubscript{3}, has been the subject of extensive theoretical and experimental studies for more than three decades. It is considered as the prototype compound, that undergoes a Mott–Hubbard transition \cite{1, 2} in its purest form. Indeed, the high-temperature ($T > T_{\text{Néel}}$) metal–insulator transition upon chemical substitution, (V\textsubscript{1–x}Cr\textsubscript{x})\textsubscript{2}O\textsubscript{3}, is isostructural and no magnetic order is acquired. Early theoretical approaches resorted to the Hubbard model to explain the electronic properties of V\textsubscript{2}O\textsubscript{3}. However, over the years, experiments indicated that the physics of this material is more involved and a realistic multi-orbital setup is needed for the complexity of the correlation effects taking place (for reviews see e.g. \cite{1–3}).

The field of correlated materials gained major momentum from the development of dynamical mean field theory (DMFT) \cite{4}. In combination with standard density functional based methods like the local density approximation (LDA) the calculation of spectral properties of materials with strong electronic Coulomb interactions became possible. Over the past years, LDA + DMFT increased our understanding of materials such as transition metals, their oxides or sulfides, as well as f-electron compounds \cite{5}. Several works highlighted the applicability of the technique to V\textsubscript{2}O\textsubscript{3} \cite{6–11}. In our previous work \cite{11}, we find that the metal–insulator transition is not due to the Brinkman–Rice mechanism \cite{12} in its single-band form, but results from the impact of Coulomb correlations on the crystal-field splitting. Owing to its octahedral oxygen surroundings, the vanadium 3d orbitals split into two e\textsubscript{g} orbitals and three lower lying t\textsubscript{2g} orbitals. The two manifolds of bands are isolated in energy, both from each other and from other orbitals. The trigonal part of the crystal field further splits the t\textsubscript{2g} into an a\textsubscript{1g} and two lower lying degenerate e\textsubscript{g} orbitals. The local Coulomb correlations result in an increased a\textsubscript{1g}–e\textsubscript{g} splitting with respect to the LDA, causing a charge transfer that pushes a\textsubscript{1g} spectral weight above the Fermi level. By computing momentum-resolved spectral functions \cite{13, 14, 11}, we made explicit predictions for angle-resolved photoemission experiments. Recent measurements on (V\textsubscript{1–x}Cr\textsubscript{x})\textsubscript{2}O\textsubscript{3} ($x = 0.011$) \cite{15} nicely agree with the theoretical spectra, further validating our current understanding of this compound.

2. Optical properties—prelude
Optical spectroscopy is an experimental probe complementary to photoemission which is commonly analyzed in terms of the
Theoretical optical conductivity of V$_2$O$_3$ at $T = 390$ K for a light polarization $E \parallel [x \times z] = [0.13, 0.0, 0.041]$. Contributions from different energy sectors (see appendix A.2): $t_{2g} \rightarrow t_{2g}$, $t_{2g} \rightarrow e_g^o$, O2p $\rightarrow t_{2g}$.

Our calculation of the optical conductivity is based on a realistic multi-band setup. At high energies, we see that both the onset and the shape of the theoretical conductivity resembles the polycrystalline conductivity, but the absolute values differ. As to the single crystal one, we note that the order of magnitude compares favorably, while the shape tends to be comparable with the high temperature curves only.

Before turning to a more detailed analysis of the different orbital contributions we compare our results to experimental data (see figure 2). First, we notice the discrepancies between the experiments: recent measurements on single crystals [24] agree well with previous single crystal experiments [20], but they are at variance with measurements using a polycrystalline film [23]. While the use of polycrystalline samples, especially in a metal, might be an issue, so is the fact that both single crystal experiments were performed up to energies of only a few eV although the extraction of the conductivity involves a Kramers–Kronig transform. The low energy shape of the theoretical conductivity resembles the polycrystalline conductivity, but the absolute values differ. As to the single crystal one, we note that the order of magnitude compares favorably, while the shape tends to be comparable with the high temperature curves only.

At high energies, we see that both the onset and the shape of oxygen 2p derived contributions agree with experiment. The upfolding scheme that uses the 2p bands from LDA is downfolded to the vanadium t$_{2g}$ orbitals. Since optical contributions from different energy sectors (see appendix A.2): $t_{2g} \rightarrow t_{2g}$, $t_{2g} \rightarrow e_g^o$, O2p $\rightarrow t_{2g}$, no identification of particular structures is possible. This calls for an upfolding scheme that includes higher energy states on the LDA level. Details are summarized in appendix A.2.

Figure 1 shows our theoretical optical conductivity for V$_2$O$_3$ at $T = 390$ K for the indicated light polarization. While in the Kohn–Sham spectrum, the t$_{2g}$ and e$_g^o$ bands are well separated, the correlations—accounted for by LDA + DMFT for the t$_{2g}$ orbitals only [11]—result in an intra-t$_{2g}$ conductivity that has weight up to energies well beyond the onset of transitions into the e$_g^o$ at about 2 eV. Contributions stemming from transitions from the occupied oxygen 2p orbitals into the t$_{2g}$ occur from around 3.5 eV onwards.

In their pioneering work, Rozenberg et al [20] analyzed the optical conductivity of V$_2$O$_3$ from the model perspective. It was concluded that the phenomenology of the temperature dependence in the conductivity can be understood by appealing to the physics of the one-band Hubbard model. In the current work, we will substantiate and extend these observations, based on a realistic multi-band setup.

### 3. Optical properties—results

Our calculation of the optical conductivity is based on the previous LDA + DMFT electronic structure computation of [11], which used a one-particle Hamiltonian that was downfolded to the vanadium t$_{2g}$ orbitals. Since optical transitions into e$_g^o$ orbitals: compared with experiment [23], we realize that the spectral weight is too sharply defined and no identification of particular structures is possible. This calls

$$\text{Re} \sigma_{\alpha\beta}(\omega) = \frac{2\pi e^2 \hbar}{V} \sum_k \int d\omega' \frac{f(\omega') - f(\omega' + \omega)}{\omega} \text{tr}[A_k(\omega' + \omega)\gamma_{k,\alpha}A_k(\omega)\gamma_{k,\beta}]$$

(1)

that is given by a convolution of spectral functions $A_k(\omega)$.

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for an LDA + DMFT calculation that includes all vanadium 3d orbitals.

We now turn to a detailed analysis of orbital effects in the optical conductivity. This is a topic that has not been dealt with so far, since previous work neglected inter-band transitions altogether [24].

At low energy only a small Drude-like tail appears. This can be understood from the underlying electronic structure. Indeed, the metallic character of V$_2$O$_3$ is mainly a result of a$_{1g}$ charge carriers that have spectral weight at the Fermi level only in a very limited region of the Brillouin zone (BZ), as can be seen in figure 4 of [11].

As can also be inferred from that work, the local spectral functions of a$_{1g}$ and e$_g^*$ character display a pseudo-gap-like behavior, and peak at finite energies rather than at the Fermi level, accounting for the feature seen at 0.5 eV in the conductivity. The latter originates from two types of transitions$: at energies lower than 0.6 eV the spectral weight is mainly due to transitions from a$_{1g}$ into low lying e$_g^*$ orbitals, that are restricted to a small region in the BZ, whereas at slightly higher energies, 0.6 eV and above, the majority of contributions derive from e$_g^*$ to e$_g^*$ transitions, which are possible in a wide region of the BZ, yet are less prominent at the $\Gamma$-point.

At this point we again use our knowledge about the electronic structure of the compound: Poteryaev et al [11] established an important orbital dependence of the quasi-particle coherence scale. Indeed, down to 390 K, e$_g^*$ excitations are far from being coherent: the imaginary part of the e$_g^*$ self-energy reaches $\sim$0.45 eV at the Fermi level, while a$_{1g}$ excitations have reached their coherence regime in our calculation [11, 3]. Thus (e$_g^*$) a$_{1g}$ carriers are (not) particularly sensitive to changes in temperature. As discussed above, the low energy ($<0.6$ eV) optical response is determined by a$_{1g}$–e$_g^*$ transitions, while above 0.6 eV e$_g^*$–e$_g^*$ transitions become dominant. Given these two facts, one can—even without explicit calculations—make some predictions about the behavior of the optical response when the temperature is raised: upon heating, the purely e$_g^*$-derived contributions will not change as much as will those that involve the a$_{1g}$ orbitals, so that the low energy response will be more sensitive than the weight beyond 0.6 eV. In particular, a broadening (and thus reduction in height) is expected for the very low energy part. This gives a natural explanation for the dip behavior that is observed in the experiments when the temperature is raised above $\sim$450 K (see figure 1 in [24] or our figure 2)$. Explicit calculations as a function of temperature (including inter-band transitions) would be desirable to confirm the picture emerging from our results. This challenging project is left for future work.

In figure 3 we show theoretical results for the insulator (V$_{1-x}$Cr$_x$)$_2$O$_3$ ($x = 3.8\%$). As discussed previously [11], we have low but finite spectral weight at the Fermi level, which results in some optical weight at low frequency. Unfortunately, no experimental data are available for this composition. Compared with pure V$_2$O$_3$, we note the suppression of low energy spectral weight and the clear distinction of transitions into the t$_{2g}$ upper Hubbard bands at $\sim$4 eV.

4. Conclusions

In conclusion, we have presented calculations of the optical conductivity of V$_2$O$_3$ in its paramagnetic phases using the generalized Peierls approach. We obtain good agreement with experiment and propose an explanation for the experimentally shown temperature dependence of the response as a signature of the orbital-selective coherence of the system. Our upfolding scheme to include higher energy orbitals captures well the transitions involving oxygen states, but reveals the necessity of including all 3d orbitals in a LDA + DMFT electronic structure calculation for this compound.

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$^5$ The following is inferred from ‘momentum-resolved optics’, i.e. from distinguishing contributions of different points in the Brillouin zone (not shown, see [3]).

$^6$ Reference [24] has invoked the change of the lattice constants upon heating in order to explain this dip. It is clear that the mechanism based on the orbital-selective coherence that emerges from our work could not have been observed in the calculation of Baldaasare et al since, there, inter-band transitions were neglected (see their footnote 26 and our discussion in appendix A.1).
Appendix. Details of the formalism

A.1. Generalized Peierls substitution approach to Fermi velocities

The Fermi velocities in (1) are given by elements of the momentum operator $\mathcal{P}$:

$$v_{k,\alpha}^{LL} = \frac{1}{m}(kL' | \mathcal{P}_{\alpha} | kL) \quad (A.1)$$

$L = (n, l, m, \gamma)$ and $\gamma$ labels atoms in the unit-cell. Equation (A.1) is easily calculated in plane waves, while using a localized Wannier-like basis $\chi_{RL}(r) = \langle r | R_L \rangle = \sum_k \exp(-ikR \cdot kL)$ renders the evaluation tedious. Inspired by the Peierls substitution approach [16] for lattice models, we can separate the above into [3, 18, 19]:

$$v_{k,\alpha}^{LL} = \frac{1}{\hbar} (\partial_{k\alpha} H_{k}^{LL} - i (\rho_{kL}^{\alpha} - \rho_{Lk}^{\alpha}) H_{k}^{LL}) + \mathcal{F}_H[\chi_{RL}]. \quad (A.2)$$

The terms in brackets are the Fermi velocity in the Peiers approximation, which is here generalised to a multi-atomic unit-cell; $\rho_{Lk}^{\alpha}$ is the $\alpha$-component of the position of atom $\gamma$ within the unit-cell. This velocity is easy to calculate since $\mathcal{F}_H[\chi_{RL}]$ reduces to intra-atoms contributions in the limit of strongly localized orbitals $\chi_{RL}$ [3], which makes the generalized Peierls velocity a good approximation for 3d and 4f systems for example.

Finally, we ask if the computation of the Fermi velocities is really necessary in practice, or if one could also resort to a simpler approximation consisting of simply omitting the Fermi velocities. Due to its simplicity, this approximation is in fact relatively popular for obtaining qualitative trends of optical properties in correlated systems [24, 25]. Since the conductivity is then a simple convolution of spectral functions, inter-band transitions ($L \neq L'$) are neglected and intra-band transitions not properly weighted. As an illustration, we show in figure A.1 a comparison of the optical conductivity calculated within the generalized Peierls formalism compared to the one computed from the simple convolution of spectral functions\(^7\): besides the obvious discrepancy in absolute value, omitting the Fermi velocities results in a noticeable change in shape too. This is owing to the momentum dependence of the matrix elements that favors certain regions in the Brillouin zone while attenuating others.

A.2. Upfolding scheme for higher energy transitions

Although the treatment of many-body correlations can often be cast into an effective low energy, downfolded system, the range of its validity is usually far exceeded by optical measurements. Thus it is desirable to allow for optical transitions into higher energy orbitals. Also, the computation of the Fermi velocities and the downfolding procedure do not commute [16], and hence it makes a difference to which Hamiltonian the generalized Peierls approach is applied. As a matter of fact, the Wannier functions of a full Hamiltonian are more localized than those of the downfolded one, whereby the Peierls approximation becomes more accurate\(^8\). The key quantity for the conductivity is the orbital trace in (1). For any unitary transformation $U_k$ holds

$$\text{tr}(v_k A_k(\omega') v_k A_k(\omega + \omega')) = \text{tr}(U_k^\dagger v_k U_k A_k(\omega') U_k^\dagger v_k U_k A_k(\omega + \omega')) \quad (A.3)$$

where we defined $\tilde{A}_k = U_k^\dagger A_k U_k$. In the case of a pure band-structure calculation (no self-energy), we can choose the transformation such that it performs the downfolding, i.e. the spectral functions $\tilde{A}_k$ acquire a block-diagonal form. We shall distinguish between the low energy ($\mathcal{L}$) and the high energy block ($\mathcal{H}$): an LDA + DMFT calculation will add local Coulomb interactions only to the former after the block-diagonalization, which results in a self-energy that lives in this sub-block, while high energy bands remain unchanged and the block-diagonality is retained. Clearly the downfolding procedure is not exact in the many-body formalism. Indeed the matrices that block-diagonalize the true interacting system also depend on frequency, due to the dynamical nature of the self-energy. Yet, when granting the approximate validity of the downfolding, and using the $U_k$ of the band-structure calculation, we can specify

$$\tilde{v}_k = \begin{pmatrix} V_1 & W \\ W^\dagger & V_2 \end{pmatrix}, \quad \tilde{A}_k(\omega') = \begin{pmatrix} L & 0 \\ 0 & H \end{pmatrix},$$

$$\tilde{A}_k(\omega + \omega') = \begin{pmatrix} \tilde{L} & 0 \\ 0 & \tilde{H} \end{pmatrix} \quad (A.4)$$

with $\tilde{v}_k = U_k^\dagger v_k U_k$. The many-body spectra $L$, $\tilde{L}$ are substituted into the $\mathcal{L}$-sector, while $H$, $\tilde{H}$ of the $\mathcal{H}$-sector stem from the initial band-structure, and (A.3) read

$$LV_1 \tilde{L} V_1 + LW \tilde{H} W^\dagger + HV_2 \tilde{H} V_2 + H W^\dagger \tilde{L} W. \quad (A.5)$$

For transitions within the $\mathcal{L}$-block, the velocity $V_1$ appears, which is the $\mathcal{L}$-block of the transformed velocity. It is

\(^7\) In order to have comparable scales, we chose for the latter case $v_k = r_0 L$, with the Bohr radius $r_0$.

\(^8\) Indeed the downfolding can be viewed as a unitary transformation that block-diagonalizes the Hamiltonian (see below). The change in accuracy manifests itself in the basis dependence of the optical conductivity within the Peierls approach.
different from the element computed after the downfolding. With the above, we moreover include transitions from, to and within the high energy block. Comparison to experiments then allows one to assess whether correlation effects substantially modify the spectrum of downfolded orbitals as well, or whether for them the initial band-structure is satisfying (see above for the V2O3 case).

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9 We can thus distinguish different origins of spectral weight. Yet we cannot tell apart contributions within the J-band. While one can suppress selected transitions by setting Fermi-velocity matrix elements to zero, contributions are in that case not additive.