Orbital selective insulator-metal transition in $\text{V}_2\text{O}_3$ under external pressure

M. S. Laad$^1$, L. Craco$^2$ and E. Müller-Hartmann$^2$

$^1$Department of Physics, Loughborough University, LE11 3TU, UK
$^2$Institut für Theoretische Physik, Universität zu Köln, 77 Zülpicher Strasse, D-50937 Köln, Germany

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We present a detailed account of the physics of Vanadium sesquioxide ($\text{V}_2\text{O}_3$), a benchmark system for studying correlation induced metal-insulator transition(s). Based on a detailed perusal of a wide range of experimental data, we stress the importance of multi-orbital Coulomb interactions in concert with first-principles LDA bandstructure for a consistent understanding of the PI-PM MIT under pressure. Using LDA+DMFT, we show how the MIT is of the orbital selective type, driven by large changes in dynamical spectral weight in response to small changes in trigonal field splitting under pressure. Very good quantitative agreement with (i) the switch of orbital occupation and (ii) $S = 1$ at each $V^{3+}$ site across the MIT, and (iii) carrier effective mass in the PM phase, is obtained. Finally, using the LDA+DMFT solution, we have estimated screening induced renormalisation of the local, multi-orbital Coulomb interactions. Computation of the one-particle spectral function using these screened values is shown to be in excellent quantitative agreement with very recent experimental (PES and XAS) results. These findings provide strong support for an orbital-selective Mott transition in paramagnetic $\text{V}_2\text{O}_3$.

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I. INTRODUCTION

Correlation driven metal insulator transitions have remained unsolved problems of solid state theory of electrons in solids for more than five decades. The pioneering work of Mott,$^1$ and of Gutzwiller,$^2$ Kanamori,$^3$ and Hubbard$^4$ involved a detailed exposition of the view suggesting that description of such phenomena lay outside the framework of band theory. Subsequent, more recent developments, including discovery of high-$T_c$ superconductors, rare-earth based systems, colossal magnetoresistive oxides along with whole families of other systems have shown that strong electronic correlations give rise to widely unanticipated, fundamentally new types of metallic behaviors, namely, non-Fermi liquid metals. A host of very careful studies now clearly show that these anomalous responses seem to be correlated with the existence of a correlated metallic state on the border of a Mott insulator in $d$-band oxides,$^5$ or to a metallic state in proximity to a localisation-delocalisation transition of $f$-electrons in rare-earth compounds.$^6$

The corundum lattice-based transition metal oxide system vanadium sesquioxide ($\text{V}_2\text{O}_3$) has been of interest for more than five decades as a classic (and now a textbook) case of an electronic system with $S = 1/2$ local moments at each site exhibiting the phenomenon of the correlation-driven Mott-Hubbard metal-insulator transition.$^1,4$ Widely accepted wisdom has it that this is one of the few cases where modelling in terms of a simple one-band Hubbard model is appropriate. Over the last few years, experimental and theoretical work has forced a revision of this view, leading on the one hand to a spurt of new approaches, and on the other to an expansion of our perception of what is new and important in the physics of TM-oxides in general. Specifically, taken by themselves as well as in combination with properties of other systems like ruthenates, CMR manganites, etc, these new studies force one to refocus the attention in terms of the strong coupling and interplay of spin and orbital degrees of freedom (not to be confused with the usual spin-orbit coupling, though that may also be relevant in some situations) and of their combined influence on the nature of charge and spin dynamics in TM oxides.

In what follows, we aim to present a far from complete view of the questions which are posed by these new studies. Focusing our attention to the early vanadium oxides, $\text{V}_2\text{O}_3$, we will start with a somewhat detailed perusal of earlier work, review key recent experiments, and follow them up with a discussion of their implications for theory. Finally, we will suggest a rather detailed scenario for correlation-induced metal insulator transitions in $\text{V}_2\text{O}_3$ that ties together essential experimental constraints in one picture. In doing so, we will give a detailed description of our theoretical modelling using a combination of the local density approximation (LDA) combined with multi-orbital dynamical mean field theory (DMFT) using the iterated perturbation theory (LDA) as the “impurity” solver.

In the first part, we will confine ourselves to summarizing known -and not so well-known experimental results on the effect of external pressure and Cr doping on the thermodynamic and transport properties of $\text{V}_2\text{O}_3$ along with the magnetic and orbital structure (and their changes) across the metal insulator transition.

In the second part, we will first review the earlier theories for the MIT in terms of the one-band Hubbard model as well as the more recent multiband Hubbard model (which allows a description in terms of a $S = 1$ model). Finally, we will propose a new scenario: one where the abrupt change in the character of spin (and presumably also orbital) correlations across the MIT is described within the strong correlation scenario. In par-
ticular, we will show how a two-fluid (i.e., orbitally selective) description can be derived from first principles, and demonstrate how the properties of V$_2$O$_3$ can be understood in this scenario.

II. EXPERIMENTAL REVIEW

The magnetic structure of V$_2$O$_3$ has been measured a long time ago. Its interpretation has however remained a subject of controversy. The robust aspects are: the antiferro-insulator (AFI) is characterized by AF order which spontaneously breaks the crystal symmetry of the corundum lattice -and in modern parlance, it corresponds to the C-type AF order with one F and two AF bonds in the hexagonal plane. The vertical V-V pairs (with V$^{3+}$) form dimers in the solid; these are aligned antiferromagnetically with the inplane V-V pairs, and ferromagnetically with other vertical V-V pairs. In terms of these dimers, the corundum lattice can be viewed as a distorted simple cubic lattice. Based on the $S = 1/2$ picture of Castellani et al., the spin waves were “characterized” in terms of a Heisenberg-like model. This was a commonly accepted picture for almost two decades, until recent experimental results forced one to reanalyze it. These are:

(i) Change of magnetic correlations across the AFI to AF-metal (AFM) phase transition in V$_{2-y}$O$_y$. In a one-band Hubbard model scenario, one would expect that the magnetic correlations in the AFI should be a remnant of those in the AFI, for e.g. broadened spin-waves of the AFI. However, measurements revealed, surprisingly, that the transport and thermodynamics is due to onset of magnetic order which seems to be totally unrelated to that in the AFI. The AFI is characterized by incommensurate order with $Q$\|c, in contrast to that for the AFI, characterized by $Q = (1/2, 1/2, 0)$ (hexagonal notation). This order in the metal is reminiscent of a small-moment SDW derived from a Fermi surface instability. Constant energy scans in INS also show that the magnetic fluctuations are far from conventional spin-waves; they are more reminiscent of particle-hole modes with extremely small correlation length of about 14 Å, much smaller than that characterizing the spin-waves in the AFI. Finally, the AFI-PI transition (P meaning paramagnetic) occurring around $T_c = 150$K is second order, once again accompanied by an abrupt change in short-ranged spin correlations. An interesting correlation concerns the change of lattice structure from monoclinic (AFI) to corundum (PI,PM), and may be linked to a change in orbital correlations.

Further, abrupt jump of the crystal volume (without change of symmetry) is also observed across the PI-PM transition at higher $T$. The $c$-axis distance decreases abruptly at the PI-PM transition, while the $a$-axis distance slightly increases, and this change needs to be correlated with the conductivity jump at the transition (see below).

(ii) Recent X-ray experiments by Park et al. have revealed the existence of an admixture of $(e_{g,1}^z, e_{g,2}^z)$ and $(e_{g,1}^z, a_{1g})$ with $i = 1, 2$ and a spin $S = 1$ on each V site, in contrast to the $S = 1/2$ proposed in Ref. 8. In addition, large differences in their ratio have been found in the AFI, PI and PM phases. In particular, this ratio is $(e_{g,1}^z, e_{g,2}^z) : (e_{g,1}^z, a_{1g}) = 2 : 1$ in the AFI, $1.5 : 1$ in the PI and $1 : 1$ in the PM phase. The AFI phase is also characterized by a monoclinic distortion involving a uniform rotation of all the V-V pairs, an observation which puts specific constraints on possible orbital order in the AFI. However, the corundum structure is recovered in the PI phase. (Does this change involve switching of the orbital correlations across AFI-PI boundary, and if so, how?) Based on this, Ezhev et al. have proposed a $S = 1$ model without orbital degeneracy as an alternative starting point to Ref. 8. More studies along this line have been done by Tanaka. An alternative point of view by Shiiina et al. pictures the AFI as a C-type AF ordered state with $S = 2$ and ferroorbital ordering.

(iii) Starting point should involve $S = 1$, suggesting use of multiband models is necessary to describe V$_2$O$_3$. In orbitally degenerate cases, the ground state is simultaneously spin and orbital ordered, and the strong coupling between the elementary excitations involving both spin and orbital flips is expected to result in emergence of qualitatively new behavior (not, however, if the scenario of Ref. 11 is taken to be valid). It is important to notice that even in the para-orbital/magnetic state(s), additional strong scattering resulting from coupled spin and orbital fluctuations might cause pronounced deviations from expectations based on (correlated) Fermi liquid theory.

(iv) Notice that this change of orbital occupation also implies an important role for the trigonal distortion (this would act like an external field in orbital pseudospin space). This quantity determines the occupation of the relevant orbitals, and in a coupled spin-orbital system, determines the effective exchange interactions (and hence the magnetic structure). In fact, the importance of this quantity, and its pressure (strain) dependence, has been identified in many members of the corundum based oxides (Fe$_3$O$_5$ in connection with the Morin or the strain-induced spin-flop transition, Cr$_2$O$_3$, in the same connection, Ti$_2$O$_3$ as manifested by an anomaly in the
$T$-dependence of the $A_{1g}$ phonon frequency across the MIT, suggesting a related common origin of the varied manifestations observed in this structurally related class of oxides.

→ It might be interesting to look at possible anomalies of the $A_{1g}$-mode frequency in Raman scattering measurements across the P-MIT in V$_2$O$_3$.

(iii) Resonant X-ray scattering (RXS) measurements at the V K-edge have been performed by Paolasini et al.\textsuperscript{15} The resonant Bragg peaks observed in the AFI phase are interpreted in terms of a 3d orbital ordering. However, the authors of Ref. 15 interpreted their results within the picture of Castellani et al., leading to difficulties with (i) and (ii).

→ One requires a re-interpretation in a way consistent with (i) and (ii), for e.g., see Mila et al. An Aside: Is the Kugel-Khomskii type of modelling required for the AFI?

(iv) Finally, Lovesey et al.\textsuperscript{16} argue that the resonant Bragg peaks arise due to ordered orbital magnetic moments of the V ions. Indeed, a large orbital contribution $M_L/M_S \simeq -0.3$ to the total magnetic moment was claimed in Ref. 16. If correct, the effect of spin-orbit coupling might become important, as argued in Ref. 11. On the other hand, if the spin-orbit coupling leads to small effects on the electronic structure, a re-interpretation would be in order.

→ How important is the role of spin-orbit coupling in the AFI phase?

(v) Optical spectroscopy provides a detailed picture of charge dynamics. Careful studies by Thomas et al.\textsuperscript{17} reveal all the characteristics of a strongly correlated system: an ”upper Hubbard band” (UHB) feature with a threshold in the AFI (and PI), and a sharp, quasicoherent feature, along with an intense mid-infra-red peak and the remnant of the UHB on the PM side. Calculations within the framework of a $S = 1/2$, one-band Hubbard model\textsuperscript{18} claim to obtain very good agreement with the observed spectra. However, to achieve this, the Hubbard $U$ has to be changed by a factor of 2 on going from the PI to the PM state, which is hardly conceivable. Alternatively, the effective hopping, or the degree of itinerance, should increase in the metallic state, leading to a change in the effective $U/t$ value, and, as is ubiquitous in strongly correlated scenarios, to a large transfer of spectral weight. In particular, given (i) – (iii), this should involve carriers coupled to spin-orbital degrees of freedom along with the concomitant lattice distortion.

→ What is the specific nature of the correlation between the change in spin-orbital correlations across the MIT and the tendency to increased itinerance which drives this transition? In particular, is the abrupt change in the $e_g^\pi e_g^\pi : t_{2g}^\pi t_{2g}^\pi$ ratio related to increase in carrier concentration or the carrier mobility (kinetic energy)? Notice that (see below) the dc transport data can be reconciled with increase in the carrier density,\textsuperscript{20} so this is an important point deserving more attention. Obviously, to make a plausible correlation between the two requires experimental characterization, as well as a proper treatment of these coupled correlations.

(vi) Photoemission Spectroscopy (PES)\textsuperscript{21} reveals further proof of the correlation-driven character of the insulator-metal transition. At high $T$, the data is claimed to be consistent with a “thermally smeared quasicoherent” peak, something within reach of single-site theories. However, it is more conceivable that strong inelastic scattering from coupled spin-orbital excitations gives rise to non-quasiparticle dynamics in the PM phase. At lower $T$, appreciable changes are observed in the PES spectra across the AFI/PM and PI/PM transitions, with the characteristic transfer of spectral weight from high to low energy over a scale of almost 4 eV (notice that $T_{MI} \simeq 300$K) implying a drastic rearrangement of electronic states over a wide energy scale.\textsuperscript{22} In the PM state, the PES spectrum shows the asymmetric two-peak structure with a Fermi edge (but we draw attention to the fact that this low-energy ”peak” is anomalously broad, suggesting non-quasiparticle dynamics), while a clear opening of a spectral gap ($E_g$) occurs in the AFI and PI phases. In the AFI phase, $E_g^{AFI} \simeq 0.3$eV, while for the PI, $E_g^{PI} \simeq 0.23$eV, with a more symmetric lineshape.

Earlier PES studies across the PI-PM transition have been controversial; in particular, the question of the $T$-dependence of the low energy spectral weight was not settled till recently. Quite recently, this question has been answered by the Michigan group,\textsuperscript{23} and the $T$-dependent renormalized, and heavily damped “quasiparticle” contribution has indeed been observed.

Details of the PES spectra at high $T$ are seemingly well captured by a DMFT applied to a multiband Hubbard model in combination with the actual LDA bandstructure (see below for more details).\textsuperscript{22} There are still some discrepancies between LDA+DMFT and experiment at lower $T < 400$ K, however; the “quasiparticle peak” is too broad by a factor of $2 - 3$, and the details of the PES lineshape in the PI still remain to be calculated. It is possible that screening-induced renormalization of $U$, etc. needs to be included; however, it is a very difficult task to do this from an ab initio starting point. Alternatively, or in concert with the above, the dynamical effect of intersite correlations might be expected to become increasingly important at lower $T$. Such effects are out of scope of LDA+DMFT, and require extensions to treat dynamical effects of spatial correlations, a more demanding task.

Given this, the interpretation of the PES spectrum will also need a re-examination. In particular, the possible importance of short-ranged spin-orbital correlations might be required to understand the anomalously broad, low-energy feature observed in PES in the PM phase.

In a coupled spin-orbital system, the degree of itinerance is directly related to changes in spin and orbital correlations coupled to possible structural changes. In course of its hopping motion, an electron is scattered by coupled spin-orbital excitations, i.e., by simultaneous flipping of spin and orbital pseudospins. In the AFI, this is
not enough to destroy AF/O order (O meaning orbital). An understanding of the change in AF/O correlations across the MIT is necessary to understand the enhancement of itinerance. In particular, within the framework of Shina et al., do the changes involve a cooperative melting of the AF/O order of the AFI? How does one then try to understand the PI/PM transition?

(vii) One of the most spectacular hallmarks of the I-M transition in V$_2$O$_3$ is the sharp jump in conductivity by seven orders of magnitude! Is the jump of $\sigma(T)$ driven by a jump in the carrier density at the transition, or by an increase in the mobility? Hall effect measurements would be a probe to answer this question (complications due to possible relevance of spin-orbit coupling, if important). On the barely metallic (close to the AFI) side (V$_{2-\gamma}$O$_3$), the Hall constant $R_H(T)$ shows behavior reminiscent of the cuprates; it is strongly $T$-dependent, increasing with decreasing $T$ with a peak around the AF ordering temperature, followed by a drop at lower $T$. The $T$-dependence gets weaker with increasing metallic-ity ($y$). More similarities with the normal state of the high-$T_c$ cuprates are seen in the different $T$ dependences of $\rho(T) \simeq T^{3/2}$ and cot $\theta_H(T) \simeq aT^2 + b$ for small $y$, which evolves into more conventional FL behavior with increasing $y$. Such a behavior would mandate strong local moment scattering in the metallic phase. Given the strong correlation signatures observed globally, a description in terms of vagaries of the Fermi surface is untenable.

→ Does the I-M transition involve a jump in the carrier density?

→ How does one understand the anomalous features of the Hall data near the MIT? In particular, similarity to cuprates suggests that such anomalies might be more general manifestations of the breakdown of Fermi-liquid theory (FLT) near the Mott transition to a Mott-Hubbard antiferromagnet, as opposed to a Slater antiferromagnet. The observation of overdamped spin waves with extremely short correlation length and anomalously broad linewidth is also reconcilable in terms of a strong scattering scenario.

A. Summary of experimental results

In conclusion, experimental results reveal very interesting points concerning the nature of the ground states and collective excitations in the different phases of V$_2$O$_3$.

1. In the AFI phase

(i) C-type AF order with ferro-type concomitant orbital order. In terms of the V-V pairs, it corresponds to C-type AF order on a distorted simple cubic lattice. A Kugel-Khomskii type of model is required to derive the AF/FO order. The picture requires consistency with $S = 1$ at each V site, and with a mixture of $(e_g^\pi, e_g^\sigma)$ and $(e_{g^\prime}, a_{1g})$ on each V-V pair.

(ii) Spin wave spectra in the insulator should be consistent with exchange constants $(J_{ij}^{ab})$ set by the FO order (FO order is consistent with the monoclinic distortion involving uniform rotation of all V-V pairs in the AFI). Also (see Mila et al.), it can be reconciled with anomalous X-ray scattering results.

2. In the PM phase

(i) no AF order (not even a remnant of AF-LRO of the AFI). I-M transition strongly first order. A jump in the $(e_g^\pi, e_g^\sigma) : (e_{g^\prime}, a_{1g})$ from 2 : 1 to roughly 1 : 1 implying a drastic rearrangement of orbital occupation (leading to para-orbital state?) across the I-M transition. The basic dependence of $J_{ij}^{ab}$ on orbital occupation and symmetry modifies these as a consequence. Recovery of the corundum structure in an abrupt way.

(ii) Strong correlation driven physics as very clearly seen in optics and PES. Since $U, U'$, $J_H$ are not likely to vary much across the MIT, the modification of hopping in a way consistent with (i) holds the key to increased itinerance. In any case, screening induced renormalisation of $U, U'$ will occur only after the system has undergone an insulator-metal transition, and it is hard to understand how the transition itself can be “derived” by reducing $U, U'$ in the PI phase.

3. In the AFM phase

(i) Non-FL features observed in transport studies in the AF-M phase, showing partial similarity to those observed in near-optimally doped cuprate superconductors raises interesting issues. Is this one of the elusive examples of spin-charge separated metallic state in a three-dimensional oxide?

In a multi-orbital Mott-Hubbard scenario, strong coupling to coupled orbital-spin excitations should lead to a dynamically fluctuating hopping, leading to inhibition of AF-LRO and to strongly reduced coherence, manifested by a low Fermi temperature. The simultaneous observation of overdamped spin waves would also follow from such kind of effects.

B. Implications for Theory

A theoretical picture of the MIT in V$_2$O$_3$ must address these issues in a consistent way. Given that much more is known about the para-orbital, paramagnetic state, as well as the view that understanding the AFI-AFM MIT requires a good knowledge of the PI, we focus our attention on the para-insulating/para-metallic states. A complete understanding of the anomalous features near
the AF-I/AF-M phase is beyond current theoretical capacity.

Castellani et al.\textsuperscript{8} started with a single c-axis V-V pair in the real crystal structure (RCS) of V\textsubscript{2}O\textsubscript{3}, and solved the two-site cluster including \(U, U'\) and \(J_{H}\). They assumed that screening processes reduce the values of these parameters, and, in particular, that \(J_{H} \simeq 0.1U\). With this choice, and in the situation where the \(t_{2g}\) levels were split into an \(a_{1g}\) singlet and \(e_{g}\) doublet by the trigonal distortion, they found that the two electrons in the \(a_{1g}\) orbitals on the pair form a total spin singlet, while the second electron populates the \(E_{g}\) states. The resulting model is clearly a \(S = 1/2\), two-orbital Hubbard model, with an orbital ordered, spin AF ground state. Based on this picture, the one-band Hubbard model was studied extensively for twenty years with a variety of techniques.\textsuperscript{25} As is clear from the earlier discussion, a variety of recent results run into direct conflict with the one-band modelling.

Theoretically, the discrepancy has to do with the fact that \(J_{H}\), which controls the spin state at each V site, is very poorly screened in a solid. This implies that \(J_{H}\) in V\textsubscript{2}O\textsubscript{3} is larger than \(0.1U\), the value used by Castellani et al. Indeed, with \(J_{H} > 0.2U,\textsuperscript{13}\) the ground state has been found to have \(S = 1\), with a change to low-spin \(S = 0\) state as \(J_{H}\) is reduced towards the value used by Castellani et al.\textsuperscript{8}

Given that the occupation of the \(a_{1g}, e_{g}\) orbitals changes discontinuously at the MIT, one would expect an important role for the trigonal field (since it acts like a fictitious external field in the orbital sector). This is expected to sensitively determine the occupancy of each orbital (orbital polarisation) in much the same way as the magnetisation of a paramagnet is a function of an applied magnetic field. In particular, one expects that the lower-lying orbital(s) should be more localized in the solid \(e_{g}\), as we shall indeed find to be the case. Further, the fact that the ratio of the orbital occupations changes discontinuously at the MIT forces one to associate a corresponding change in the trigonal field as well.

On the other hand, observation of global strong correlation signatures in various phases of V\textsubscript{2}O\textsubscript{3} as described above in detail implies a fundamental inadequacy of the band description, and mandates use of a strong correlation picture.

Summarising, a consistent description of the PI/PM MIT requires a theoretically reliable description involving marriage of structural aspects (LDA) and strong correlation features (MO-DMFT).

In the rest of this paper, we confine ourselves to the theoretical description of the PI/PM Mott transition in V\textsubscript{2}O\textsubscript{3}. Starting with a detailed exposition of the LDA+DMFT(IPT) which we use as a solver (the pros and cons of using IPT vis-a-vis other impurity solvers will be discussed), we will derive a two-fluid description of the PI/PM transition in V\textsubscript{2}O\textsubscript{3} attempting to achieve an internally consistent description. Finally, a quantitatively accurate description of the one-particle spectral function across the MIT and low-\(T\) thermodynamics will be demonstrated within this scenario.

III. LDA+DMFT TECHNIQUE

As argued in detail and shown in recent work,\textsuperscript{26} LDA+DMFT has turned out to be the method of choice for a consistent theoretical description of the competition between quasi-atomic, strong Coulomb interactions (multi-orbital) and itinerance (LDA spectra, encoding structural details in the one-electron picture) in real three dimensional transition-metal and rare-earth compounds. The central difficulty in this regard has been the choice of an appropriate impurity solver to solve the multi-orbital, asymmetric Anderson impurity problem. Two ways have been used with varying degrees of success: iterated perturbation theory (IPT) and quantum Monte Carlo (QMC).

We have used multi-orbital extension of IPT to solve the impurity model. On the one hand, such an approach should be valid if the behavior of the multi-orbital SIAM is "analytic in \(U, U', J_{H}\): this is known to hold for the general asymmetric version. MO-IPT also has the advantage of being extendable to \(T = 0\), and the self-energies can be extracted at modest numerical cost. On the other hand, it is by no means exact, and calculations done for the one-band Hubbard model\textsuperscript{26} show quantitative differences between IPT and QMC results for the critical value of \(U = U_{c}\) at which the MIT occurs. It has also been claimed\textsuperscript{27} that the IPT spectral functions are very different from the QMC ones, and the latter are claimed to be more reliable vis-a-vis the true spectral function, as well as with the actual, experimentally determined spectral functions. Here, we should emphasise that the IPT results for the many body DOS are in excellent agreement with both exact diagonalisation\textsuperscript{28} as well as dynamical DMRG results for the one band Hubbard model in \(d = \infty\). While no such evidence exists for multi-orbital models, we believe that the above arguments show that IPT is a good approximation, even though it is not "numerically exact".

With these caveats, we describe our multi-orbital iterated perturbation theory (MO-IPT) for multi-band correlated systems. For early TM oxides, one-electron band-structure calculations show that, in three dimensional cases, the \(t_{2g}\) DOS is well separated from the \(e_{g}\) DOS as well as from the O-2p DOS. More precisely, the \(t_{2g}\) DOS does have contributions from components of the \(e_{g}\) and O-2p orbitals having \(t_{2g}\) orbital symmetry. Structural effects, such as those produced by trigonal crystal fields (V\textsubscript{2}O\textsubscript{3}\textsuperscript{29}) and antiferroelectric distortions (VO\textsubscript{2}\textsuperscript{30}) are adequately described by LDA. In addition, the multi-orbital Coulomb interactions are parametrised by three parameters \(U, U', J_{H}\). The Hund’s rule coupling, \(J_{H}\), is very poorly screened and can be taken equal to its atomic value. The intra-orbital (\(U\)) and inter-orbital
(\(U'\)) Coulomb interactions are screened in the actual solid: usually, their screened values have traditionally been calculated using constrained LDA. In correlated systems, this is a problem, however, as the dynamical processes screening these parameters arise from correlated electrons having dualistic (itinerant-localised) character, rather than from free band electrons. This well-known problem has received scant attention to date; indeed, we are aware of only one previous work attempting to cure this malady.\(^{31}\) Below, we will show how the renormalised \(U, U'\) are self-consistently computed in a correlated approach, and lead to a consistent description of the PES results in the PM phase.

A. The many-body Hamiltonian

Generally, the full many-body Hamiltonian for early TMOs is written as,

\[
H = \sum_{kabc\sigma}(\epsilon_{ka} + \epsilon_{k\sigma}^{0}\delta_{ab})c_{ka\sigma}^\dagger c_{k\sigma\beta} + U \sum_{ia}n_{ia\uparrow}n_{ia\downarrow} + U' \sum_{ia\neq ib}n_{ia}n_{ib} - J_H \sum_{ia\neq ib}S_{ia}S_{ib} \tag{1}
\]

where \(a, b = xy, yz, zx\) denote the three \(t_{2g}\) orbitals. Details of the actual one-electron bandstructure in the real lattice structure are encoded in the one-electron band dispersion, \(\epsilon_{ka}\): the corresponding LDA DOS is \(\rho(\omega) = N^{-1}\sum_{k} \delta(\omega - \epsilon_{ka})\). Here \(\epsilon_{ia} = \epsilon_{a} - U(n_{a\sigma} - \frac{1}{2}) + \frac{J_H}{2}\sigma(n_{a\sigma} - 1)\), where \(\epsilon_{a}\) are the on-site energies of \(t_{2g}\) orbitals within LDA and the rest of the terms are subtracted therefrom in order to avoid double-counting of interactions already treated on the average by LDA.

We emphasise that the basic method was already developed in Ref.\(^{26}\), and here, we extend this ideology using more detailed analysis to study the full one-electron spectral function in both insulating and metallic phases in \(V_2O_3\). Our strategy is:

(a) Beginning with LDA results in the real corundum lattice (see Fig. 1), derive a correlated Mott insulating state using multi-orbital DMFT with \(U = 5\ eV\), and \(U' = 3\ eV\) (we use \(J_H = 1.0\ eV\) for \(V^{3+}\)), values obtained from constrained LDA. The LDA bandwidth is \(W = 2.5\ eV\), and the bare LDA trigonal field is read off as \(\Delta = 0.32\ eV\). In what follows, we will work in the basis of LDA eigenstates which diagonalises the one-particle density matrix.

(b) Mimic the effects of external pressure by noticing that it should lead to modification of the renormalised (correlated) value of the trigonal field. In line with this ideology, first known to be propounded by Mott and co-workers, we search for the instability of the correlated (Mott insulator) solution found in (a), to a second solution of the DMFT equations as a function of \(\Delta\). We emphasise here that we do not change the bare LDA parameters: indeed, we argue that a Mott transition from a correlated insulator to correlated metal cannot be validly described by changing bare LDA parameters, since these have no clear meaning in a strongly correlated system.

(c) To provide a quantitative description of the one-electron spectral function in the metallic phase, we use the correlated (DMFT) results to compute the screening-induced reduction in \(U, U'\) in the metallic phase. This is crucial: we derive the screened \(U, U'\) in the PM phase after deriving the I-M transition, and do not derive the I-M transition itself by reducing \(U, U'\), as seemingly done in earlier work.\(^{26,32}\) Using the DMFT result, the screened \(U, U'\) are estimated by an extension of Kanamori’s \(t\)-matrix calculation to finite density.

Using the screened values of \(U, U'\) (notice that \(J_H\) is almost unaffected by screening, so we use the same value for it throughout), we compare our theoretical (correlated) DOS with PES and XAS results obtained experimentally in the PM phase.

Incorporation of electron correlations into the LDA gives rise to a two-stage renormalisation:

(1) \(U, U'\) and \(J_H\) give rise to multi-orbital Hartree shifts in the on-site orbital energies of each \(t_{2g}\) orbital. In \(V_2O_3\), the trigonal field lifts the \(t_{2g}\) degeneracy, with the lowest \(a_{1g}\) orbital \([\simeq (xy + yz + zx)]\) lying about \(\Delta = 0.32\ eV\) below the higher lying \(e_{g}^\pi\) orbitals \([\simeq (xy - yz), (2xy - yz - zx)]\) within LDA. Given this, the \(a_{1g}\) orbital is always occupied by one electron, the second residing in the \(e_{g}^\pi\) orbitals. The observation of \(S = 1\) on each V site requires strong \(J_H\), implying even stronger \(U, U'\), even in the PM phase.

Multi-orbital Hartree shifts renormalise the orbital energies:

\[
\epsilon_{a_{1g}} = \epsilon_0 + U'n_{a_{1g}}\quad \epsilon_{e_{g}^\pi} = \epsilon_0 + \Delta + U'n_{a_{1g}},
\]

where \(n_{a_{1g}} = n_{a_{1g}}\) is the \(e_{g}^\pi\) orbital occupation. These shifts correspond to effects captured by LDA+U.\(^{12}\) They

![FIG. 1. LDA partial density of states for the \(e_{g}^\pi\) (red) and \(a_{1g}\) (blue) orbitals, obtained from Ref. 32.](image-url)
do give the correct, insulating ground states (with orbital/magnetic order), but cannot describe the phase transition(s) from correlated Mott insulators to correlated metals. This can be traced back to the fact that LDA+U treats correlations on a static level, neglecting quantum nature of electron dynamics, and so cannot access the spectral weight transfer-driven physics at the heart of Mott-Hubbard transitions.

(2) In a one-electron picture, this would be the end of the story. In reality, however, hopping of an electron from a given site to its neighbor(s) is accompanied by dynamical generation of particle-hole pairs (the more, the larger $U, U'$ are), which inhibit its free band motion. Electrons can move quasicoherently by dragging their corresponding “electronic polarisation cloud” along. With increasing $U, U'$, electrons get more and more “localised”, corresponding to transfer of coherent low energy spectral weight to high-energy (quasi-atomic) incoherent regions, until the MIT, all the weight resides in the incoherent Mott-Hubbard bands. It is precisely this effect that is out of scope of LDA+U, and requires dynamical mean field theory (DMFT) for a consistent resolution.

Since the system is strongly correlated, the small changes in bare LDA parameters caused by (1) lead to large changes in transfer of dynamical spectral weight. Specifically, in systems undergoing MIT, small changes in bare LDA of lattice distortion(s) transfer high-energy spectral weight to low energies, driving the Mott transition.

B. The one-particle Green’s functions

Given the actual LDA DOS for the $t_{2g}$ orbitals (this includes the V-d orbitals and O 2p part having “$t_{2g}$” symmetry), the band Green’s functions within the LDA (in the basis which diagonalises the one-particle density matrix) are $G_{ab}(\omega) = \delta_{ab} G_0(\omega) = \delta_{ab} \frac{1}{N} \sum_k (\omega - \epsilon_{ka})^{-1}$. We define the correlated one-electron Green’s function and the associated irreducible self-energy for each orbital $a$, by $G_{a\sigma}(\omega)$ and $\Sigma_{a\sigma}(\omega)$: the two are related by the usual Dyson’s equation,

$$G^{-1}_a(\omega) = [G^0_a(\omega)]^{-1} - \Sigma_a(\omega) .$$  \hspace{1cm} (2)

It is obvious that the Green’s functions can be exactly written down for the non-interacting case, as well as for the atomic limit ($\epsilon_{ka} = 0$). In contrast to the case of the one-band Hubbard model, however, the exactly soluble atomic limit contains the local, inter-orbital correlation function, $<n_an_b>$, in addition to $<n_a>$.

1. MO-IPT: an interpolative ansatz for multi-orbital systems

In the spirit of the IPT developed by Rosenberg et al. for the one-orbital Hubbard case, we require an interpolative scheme that connects the two exactly soluble cases above, gives correlated Fermi liquid behavior in the metallic phase, and a Mott-Hubbard transition from a correlated FL metal to a Mott insulator as a function of $U, U'$ for commensurate cases. In order to achieve this, we have extended the philosophy of Ref. 35. The central requirements for a consistent interpolative scheme capable of describing all of the above are that:

(i) Formally defined one-electron Green’s function,

$$G_a(\omega) = \frac{1}{N} \sum_k \frac{1}{\omega + \mu - \epsilon_{ka} - \epsilon_{ka}}$$  \hspace{1cm} (3)

where $\epsilon_{ka}$ describes the dispersion of the LDA bands for orbitals $a, b = t_{2g}$, and the self-energy is given by

$$\Sigma_a(\omega) = \frac{\sum_b A_{ab} \Sigma^{(2)}_{ab}(\omega)}{1 - \sum_b B_{ab} \Sigma^{(2)}_{ab}(\omega)}$$  \hspace{1cm} (4)

with

$$\Sigma^{(2)}_{ab}(\omega) = \frac{U_{ab}^2}{\beta^2} \sum_{lm} g_{a}(i\omega_l) G_{b}(i\omega_m) G_{b}^0(i\omega_l + i\omega_m - i\omega)$$  \hspace{1cm} (5)

being the second-order (in $U, U'$) contribution. Here, $N_{ab} = 2$ for $a, b = e_{g1}, e_{g2}$ and 4 for $a, b = a_{1g}, e_{g1,2}$. Finally, the bath propagator is given as

$$G^0_{ab}(\omega) = \frac{1}{\omega + \mu_a - \Delta_a(\omega)},$$  \hspace{1cm} (6)

with $\Delta_a(\omega)$ interpreted as the dynamical Weiss field for orbital $a$.

(ii) The interpolative self-energy for each orbital $a$ should be chosen by fixing interpolative parameters such that the exact Friedel-Luttinger sum rule is strictly (numerically) obeyed, and,

(iii) to reproduce the Mott insulator beyond a critical coupling, a high-energy expansion around the atomic limit is performed, yielding another equation for the interpolative parameters. Here, the high-energy expansion is truncated by including only the first few terms which guarantee the exact reproduction of the first three moments of the one-electron spectral function. In contrast to the one-band case, however, the exact atomic limit for the multi-orbital case contains the local, inter-orbital correlation function, $D_{ab}[n] = <n_an_b>$. We are aware of only one earlier work$^{35}$ where $D_{ab}[n]$ is computed using the coherent potential approximation (CPA). Strictly speaking, this is an approximation to the Hubbard model(s) which is qualitatively valid in the Mott insulating state, but is known to fail in the correlated PM phase(s). This is because CPA replaces the actual, dynamical (annealed) “disorder” in the PM phase(s) by quenched, static disorder, and thus fails to capture the dynamical Kondo screening central to deriving correct (correlated) FL behaviour in the PM phase. Given this,
it is hard to identify the extent to which computed results depend upon introducing such approximations, and this should be checked carefully by comparison with calculations which compute all local correlators in a single, consistent scheme. The correct way to compute $D_{ab}[n]$ is actually not complicated within multi-orbital IPT, and is described below.

These two equations for the parameters $A_{ab}$ and $B_{ab}$ are solved to yield these as explicit functions of $U, U'$, $< n_a >$, $< n_a n_b >$ and $< n_a^0 >$ (this last average is the “effective” number of fermions in orbital $a$ corresponding to an “effective” Green’s function used in the interpolative IPT, see Refs. 35, 36). Explicitly, we have,

$$A_{ab} = \frac{n_a (1 - 2n_a) + D_{ab}[n]}{n_a^0 (1 - n_a^0)} \tag{7}$$

and

$$B_{ab} = \frac{1 + 2n_a}{U_{ab} n_a^0 (1 - n_a^0)} \tag{8}$$

where $n_a$ and $n_a^0$ are defined from the GFs $G_a(\omega)$ and $G_a^0(\omega)$. The inter-orbital correlation function $D_{ab}[n]$ is calculated from

$$D_{ab}[n] = < n_a > < n_b > + \frac{1}{U_{ab}} \int_{-\infty}^{+\infty} \Xi(\omega) f(\omega) d\omega \tag{9}$$

the last term following from the equation of motion for $G_a(\omega)$ and $G_a^0(\omega) = -\frac{1}{\pi} \text{Im} [\Sigma_a(\omega) G_a(\omega)]$.

The above equations form a closed set of coupled, non-linear equations which are solved numerically. We found fast convergence of the self-consistent system of equations, and typically twenty iterations sufficed for the parameter values considered here. The converged results allow us to study the one-particle DOS, and the corresponding orbital occupations, spin states, as well as the strength and character of local multi-orbital correlations in both PI and PM phases, as described below in detail.

**IV. RESULTS AND DISCUSSION**

In this section, we present a detailed set of results for the one-particle spectral function in both the PI and PM phases in V$_2$O$_3$. While doing so, we will make extensive contact and discuss important differences between our work here and previous results recently obtained by other authors.

In Fig. 2, we show the single particle DOS for the Mott insulator, obtained with $U = 5.0$ eV, $U' = 3.0$ eV and $J_H = 1.0$ eV as correlation parameters for this system. These are slightly different from those used in our previous work, but are roughly the same as those used by Held et al. recently. A clear Mott-Hubbard gap, $E_G = 0.2$ eV, is seen, and, as expected from the orbital assignment, the $e_g^0$ states are more localised in the solid. The renormalised trigonal field $\Delta_t = \delta_{a_{1g}} - \delta_{e_g^0} = 0.28$ eV, is read off directly from Fig. 2. The orbital occupations are computed to be $(n_{a_{1g}}, n_{e_g^0}) = (0.32, 0.34)$ in the PI, in nice agreement with XAS estimations.

We now study the paramagnetic metallic state obtained as an instability of the correlated Mott insulator derived above. In other works, the PM state is “derived” not by searching for an instability of the correlated PI state under pressure, but by computing the LDA bandstructure for the “metallic” state *without* correlations. The screened values of $U, U'$ are computed using constrained LDA, and these are then used to describe the PM phase. In reality, however, one has to study the transition to the PM phase without leaving the correlated picture, and derive the transition by searching for the second, metallic solution of the DMFT equations under pressure.

To justify our new approach, we specify the problems associated with earlier approaches: We now derive the phase transition between two strongly correlated phases by using corresponding LDA bandstructures to separately derive the two phases. This is because using changes in bare LDA parameters to study correlated phases is clearly problematic, since these parameters have no clear meaning in a correlated picture. One must use the renormalised values of these parameters instead, and these are generically modified in unknown ways by strong multi-orbital correlations. These changes in bare LDA parameters, and the modification of the response of correlated electrons to these changes, must be selfconsistently derived *within* the LDA+DMFT procedure. Clearly, this route has not been used in other approaches.

(2) It follows that an inescapable consequence of using such approaches is that the values of $U, U'$ used for the PM phase are computed using constrained LDA (i.e, using the uncorrelated bandstructure assuming that the
screening electrons are free band electrons). However, in reality, the screening electrons in the correlated PM phase have a dualistic character generic to the Mott-Hubbard character of the system. As is known from Ref.25, the electronic kinetic energy, or itinerance, is reduced in the PM phase: it is these correlated electrons which screen $U$, $U'$ in the real correlated system. In an “ab initio” treatment, the effective $U$, $U'$ should be computed using the correlated spectral functions to estimate screening. Replacement of the renormalised spectral functions by bare LDA ones will introduce an approximation, overestimating the screening of $U$, $U'$ (this is hard to quantify, but is estimated to be of order of twenty percent!).

In order to avoid these difficulties, we adopt the following strategy.

(A) We hypothesise that external pressure modifies the trigonal field. To our knowledge, this is not completely new: Mott and co-workers proposed such ideas in the seventies,1 and more recently, Tanaka made a similar hypothesis in a cluster approach for V$_2$O$_3$.11 To model this change in $\Delta_t$ under pressure, we do not change the trigonal field by hand. Rather, we input trial values of $\Delta_t$, changing it from its value in the (Mott) PI by small trial amounts, and search numerically for its critical value, $\Delta'_t$, which stabilises the second, correlated metallic solution of the DMFT equations. The new values of $\Delta_t$ in the (correlated) PM phase are again read off from the converged DOS for each orbital. We emphasise that we do not decrease $U$, $U'$ by hand, neither do we use different LDA DOS for different phases, for reasons explained before. We note that Savrasov et al.38 have employed similar ideology to study the giant volume collapse across the $\alpha-\delta$ transition in Pu.

In a strongly correlated system, small changes in the renormalised trigonal field lead to large changes in dynamical spectral weight transfer from high- to low energies, typically over a scale of a few eV. This is precisely our mechanism for the first-order Mott transition in V$_2$O$_3$ under pressure. We expect the free energy to have a double well structure. Pressure changes the trigonal field (we remind the reader that $\Delta_t$ acts like an external field in the orbital sector), lowering the second minimum (PM) relative to the first (PI) beyond $\Delta'_t$.

(B) Using the converged DOS for each orbital, the occupation(s) of various orbitals (and their changes from their PI values), the local spin value at each V site, and information about the detailed character of the PM state is directly obtained.

In Fig. 3, we show our results for the PM phase obtained within our technique. At $T = 0$, the hypothetical PM phase (it is never observed in reality) shows a sharp, quasicoherent FL resonance. We identify this feature with combined spin-orbital Kondo screening in the PM phase of a multi-orbital Hubbard model. This is easily seen as follows. To obtain a correlated Mott insulator, we need not only $U = 5.0$ eV, but also $U' \simeq (U - 2J_H) = 3.0$ eV: indeed, if $U'$ were ignored, a $t_{2g}$ electron hopping from one V site to its neighbor could always hop off like a band electron just by going into an unoccupied $t_{2g}$ orbital at that site, making a PI state impossible. Given the small spectral weight carried by this feature, we expect a low lattice coherence scale, above which the PM would be described as an incoherent metal. The trigonal field in the PM, $\Delta'_t = -0.291$ eV and the occupations of each $t_{2g}$ orbitals, $[n_{a1g}, n_{eg1}, n_{eg2} = 0.38, 0.31, 0.31]$, are read off from the converged PM solution of the DMF equations. Very satisfyingly, the spin state remains unchanged, and the orbital occupations change across the MIT in semiquantitative agreement with XAS results.10

In Figs. 4 and 5, we show the effect of finite temperature on our results. As expected on general grounds within the DMFT framework, the FL resonance is broadened by finite-$T$ and lowered in height (the pinning of the interacting DOS at $E_F$ to its LDA value, dictated by Luttinger’s theorem, holds only at $T = 0$). The effects of introducing chemical disorder in the PI is shown in Fig. 6. The results were obtained by combining multi-orbital IPT with the coherent-potential approximation (CPA).39 In agreement with very recent observations,23 we indeed observe a broadened “quasiparticle” in the PM, and closing in of the Mott gap in the PI by incoherent spectral weight transferred across large energy scales from high- to low energies. Comparing Figs. 4 and 6, it is clear that, at sufficiently high-$T$, the spectra in the chemically disordered PI and the PM phases do resemble each other qualitatively. As observed by Allen,40 this implies that there is no fundamental difference between the “metal” and “insulator” at sufficiently high $T$: this agrees with the observation that the first order Mott transition is replaced by a smooth crossover at high $T$. 

![Graphs and figures are not included in this text.]

\[\text{FIG. 3. (color online) Orbital-resolved (upper panels) and total (lower panel) one electron spectral functions for the metallic phase of V}_2\text{O}_3.\]

\[\text{Note that only the } a_{1g} \text{ orbital DOS crosses } E_F \text{ in the metallic phase; the } e_g^s \text{ orbitals still shows Mott-Hubbard insulating features, showing the “two-fluid” character of the MIT in V}_2\text{O}_3.\]
Disordered semiconductors in the past. We used phenomenologically in connection with the MIT in institutes an explicit realisation of the “two-fluid” model. This constitutes the evolution of the DOS at \(E_F\) as a function of the occupation of the \(a_{1g}\) orbital. A clear first-order I-M transition around \(n_{a_{1g}} = 0.38\) was found, involving, as described above, a discontinuous change in (self-consistently determined) occupations of each orbital. These observations are intimately linked to the multi-orbital Mott-Hubbard character of correlations in \(V_2O_3\). Polarised XAS results might already hold the clue to establishing an approximate two-fluid character of the PM phase: the \(a_{1g}\) spectral weight should dominate over the \(e_{g}^\pi\) contribution for energies up to the Mott gap. Orbital resolved optical studies could also be used to test our picture.

Strong indirect support for our picture comes from the early observation\(^9\) of an anisotropic change in the lattice constants along \(a/b\) (planar) and \(c\) axes across the P-MIT in \(V_2O_3\). Instead of a uniform volume collapse expected across the MIT,\(^41\) increase in \(a(b)\) and a decrease in \(c\) was found across the MIT. Such an anisotropic volume change across the MIT is inconsistent with simultaneous gapping of all \(t_{2g}\) orbitals (where we would expect an isotropic volume change), but is completely consistent with our (orbital selective) two-fluid picture derived above.

V. COMPARISON WITH PES AND XAS

In this section, we describe how our approach provides an excellent description of the experimental photoemission (PES) and X-ray absorption (XAS) data on \(V_2O_3\) in the PM phase. As argued before, this requires us to recompute the full one-particle local spectral function (total DOS) using values of \(U, U'\) renormalised by dynamical metallic screening in the correlated metallic phase. In order to do this, we have used an extension of Kanamori’s \(t\)-matrix approach\(^3\) to estimate these parameters.

In the multi-orbital case, this is a horrendous problem in general. Fortunately, in the effective two-fluid picture of the PM phase derived above, the general analysis can be simplified. This is because the \(e_{g}^\pi\) electrons remain “insulating”, i.e., Mott localised, up to energies of the order of the Mott-Hubbard gap. We then expect only the...
pared with experimental work

The results are recomputed the one-electron spectral function for the orbital,  

\[ \chi_{pp}(q) = -\frac{1}{N} \sum_{nmk} G_{a_{1g}}(q-k, i\omega_n - i\nu_n) G_{a_{1g}}(k, i\nu_n). \]  

(10)

In \( d = \infty \), this can be expressed as an integral over the LDA DOS and the full irreducible one-electron self-energy, permitting a direct evaluation. The onsite Hubbard \( U \) is renormalised by the local part of this susceptibility, via the equation,  

\[ U_{\text{eff}} = \frac{U}{1 + U\chi_{\text{loc}}(\omega)}. \]  

(11)

Using the relation \( U \simeq (U' + 2J_H) \), valid for \( t_{2g} \) systems, along with the fact that \( J_H \) is essentially unscreened, we estimate \( U, U' \) in the PM phase. We observe that this implies a frequency-dependent \( U_{\text{eff}} = U(\omega) \). We have found, however, on computation that the \( \omega \)-dependence is weak for energies up to the Mott gap, and so use its \( \omega = 0 \) value \( U_{\text{eff}} = U(0) \) in what follows.

![Graph showing theoretical LDA + DMFT results compared to experimental data](image)

**FIG. 7.** (color online) Comparison of theoretical LDA + DMFT result (blue) for the total one-electron spectral function in the metallic phase of V\(_2\)O\(_3\) to the experimental results taken from Refs. 21, 22 (for PES) and from Ref. 42 (for XAS).

Starting with the values of \( U, U' \) used earlier, we estimate \( \chi_{\text{loc}}(0) \simeq 0.084 \), yielding \( U_{\text{eff}} \simeq 3.5 \) eV. With \( J_H = 1.0 \) eV, this implies that \( U' \simeq 1.5 \) eV. We have recomputed the one-electron spectral function for the PM phase using these values. The results are compared with experimental work\(^{21,22,42} \) in Fig 7. Very satisfyingly, excellent quantitative agreement over almost the whole energy scale from \(-3.0 \leq \omega \leq 1.2 \) eV is clearly observed. In addition to the detailed shape of the lower Hubbard band (in PES), excellent agreement with the intense peak in XAS is also clear. Consideration of parts of the spectrum for \( \omega \leq -3.0 \) eV and \( \omega \geq 1.2 \) eV is hampered by our restriction to the \( t_{2g} \) sector in the LDA+DMFT calculations. Due to the reduction of \( U, U' \) as above, the \( t_{2g} \) orbital occupation is now \((n_{a_{1g}}, n_{eg_1}, n_{eg_2}) = (0.36, 0.32, 0.32)\), in even better agreement with XAS results\(^{10} \).

However, though good, the agreement is not quite so perfect in the low-energy region: our computed “broad” peak (ascribed to a “quasiparticle” in earlier work\(^{22} \)) is narrower than the experimental feature by a factor of 1.8. On first sight this might seem to confirm the interpretation in the earlier work. However, we observe that this feature is peaked at \( \omega \simeq -0.37 \) eV, while a clear pseudogap-like dip is resolved around \( E_F \). Hence, in our picture, the metallic phase cannot be described in a FL quasiparticle language; instead, short-lived, incoherent, non-FL pseudoparticles should dominate the PM phase. Interestingly, observation of a linear-in-\( T \) (instead of the \( T^2 \) form for a correlated FL) resistivity supports a non-FL quasiparticle interpretation. It is possible that the \( T \) regime where this is valid lies above an effective FL coherence scale (below which a \( T^2 \) term in resistivity would follow) which is masked by emergence of orbital/spin ordered insulating states at lower \( T \). At \( T > T_{\text{coh}} \), the \( dc \) resistivity is indeed linear in \( T \) in a Hubbard model framework, where it arises from inelastic scattering off unquenched spin-orbital local moments in a \( d = \infty \) multiband Hubbard model.

Our observation of a low energy pseudogap feature can be traced back to the strong bonding-antibonding splitting observed in LDA results (see Fig. 1). This is a direct consequence of strong hopping along the \( a_{1g} \) orbitals, leading to strong covalency and robust singlet character between V-V pairs along the c-axis. (see Ref. 43 for an early discussion on this point). Our analysis does partially show up the effects of strong covalency, manifested in the pseudogap feature found above. However, the fact that we can resolve most of the spectrum accurately, but fail to reproduce the correct broadening of the low-energy feature, implies that it may be necessary to explicitly consider the dynamical effects of intersite (V-V) correlations for a complete resolution of the PES spectrum, as alluded to in the experimental section. This is however out of scope of LDA+DMFT, and requires a cluster extension.

VI. CONCLUSION

In conclusion, we have studied the first-order Mott transition under pressure in V\(_2\)O\(_3\) using the state-of-the-art LDA+DMFT technique. We have proposed a new picture for the MIT, which is driven by large changes in the transfer of dynamical spectral weight (via DMFT)
accompanying small changes in the renormalised trigonal field splitting under pressure. Very good quantitative agreement with the orbital occupations, spin state of $V^{3+}$ ions, as well as effective mass enhancement in the PM state is obtained. The MIT is found to be first-order, and orbital selective (only the $a_{3g}$ DOS shows metallic behavior). Finally, using the correlated solution, we have computed the screening induced renormalisation of $U, U'$ in the PM phase. Using these, excellent quantitative agreement with the full one-particle spectral function (PES and XAS) is found in the PM phase. These findings constitute strong support for our underlying two-fluid picture, which is ultimately an interesting manifestation of strong, multi-orbital Coulomb interactions in this early transition-metal oxide.

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