Orbital Switching and the First-Order Insulator-Metal Transition in Paramagnetic $V_2O_3$

M. S. Laad, L. Craco and E. Müller-Hartmann

Institut für Theoretische Physik, Universität zu Köln, 77 Zülpicher Straße, D-50937 Köln, Germany
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The first-order metal-insulator transition (MIT) in paramagnetic $V_2O_3$ is studied within the ab-initio scheme LDA+DMFT, which merges the local density approximation (LDA) with dynamical mean field theory (DMFT). With a fixed value of the Coulomb $U = 6.0$ eV, we show how the abrupt pressure driven MIT is understood in a new picture: pressure-induced decrease of the trigonal distortion within the strong correlation scenario (which is not obtained within LDA). We find good quantitative agreement with (i) switch of the orbital occupation of $(a_{1g}, e_g^\sigma, e_g^{\pi})$ and the spin state $S = 1$ across the MIT, (ii) thermodynamics and $dc$ resistivity, and (iii) the one-electron spectral function, within this new scenario.

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The spectacular metal-insulator transition (MIT) in the paramagnetic (P) state in $V_2O_3$ has long been considered as a classic, and by now almost a textbook version of correlation-driven MIT in a one-band correlated system described by the one-band Hubbard model [1]. This conventional wisdom has been recently challenged by new experiments, clearly showing the coupled spin-orbital character of the system, and necessitating a revision in terms of a multiband picture.

The conventionally accepted picture rested upon the following argument. In the high-$T$ phase, $V_2O_3$ exists in the corundum structure, and with a 3$d^2$ state ($V^{3+}$), the two $e_g^\sigma$ orbitals are empty, while the triply degenerate $t_{2g}$ orbitals are filled by two electrons. This triple degeneracy is lifted by a small trigonal distortion, leading to a singly occupied $a_{1g}$ orbital oriented along the $c$-axis, and doubly degenerate planar $e_g^{\pi}$ orbitals, occupied by the second electron. Castellani et al. [2] proposed that strong covalent effects lead to a bonding singlet $a_{1g}$ state involving two $V$ ions along the $c$-axis. The remaining electron in the two-fold degenerate $e_g^{\pi}$ orbitals gives rise to a $S = 1/2$ model with orbital degeneracy. This inspired development of theoretical techniques, culminating in the dynamical mean field theory (DMFT) [3], leading to considerable improvement in our understanding of the MIT. Within the basic picture [2], Rozenberg et al. [4] used DMFT for one- and two-orbital Hubbard models with Bethe density-of-states to study the MIT in $V_2O_3$.

Recent polarized X-ray scattering results of Park et al. [5] require, however, an interpretation in terms of a spin $S = 1$ at each V site, with a mixed orbital $e_g^{\sigma}a_{1g}: e_g^{\pi}e_g^{\pi} = x : (1-x)$ configuration. An exciting conclusion from these results is that the above ratio changes its value abruptly at the MIT, forcing one to abandon the one-band Hubbard model to describe $V_2O_3$. Notice that this implies an important role for the trigonal splitting, since the lower-lying orbital will be more “localized” when local Coulomb interactions are switched on. This raises questions concerning a possible link between the orbital “switching” and the drastic change in the electronic state, and to a possible common underlying origin.

Thus, a consistent description of the MIT, along with an understanding of the strong correlation features requires a combination of structural aspects of $V_2O_3$ (encoded in LDA+U) with a reliable many-body theory like DMFT. In this letter, we study these questions within LDA+DMFT [3], which has been shown to provide a good quantitative $ab$-initio description of correlated electronic systems. Moreover the MIT in the P-phase has been studied [13] using LDA+DMFT(QMC). However, the link between the MIT and the abrupt switching of orbital occupation has, to our knowledge, not been explored in detail. We should mention that such a scenario may have broader application to other systems, notably in Ca$_{2-x}$Sr$_x$RuO$_4$ [14], and is a hallmark of the...
importance of orbital correlations in a system.

We start with the actual LDA bandstructure of $V_2O_3$ in the corundum structure [13]. These results represent (Fig. 1) metallic behavior, with comparable width (2.5 $eV$) for both $a_{1g}$ and $e_g^\pi$ bands, and a strongly asymmetric structure. With an onsite $U \approx 5 - 6$ $eV$, this would invalidate a MO-based approach [6]. Further from the $a_{1g} - e_g^\pi$ splitting, the trigonal field splitting is estimated to be $\approx 0.4$ $eV$. The LDA densities of states with and without the trigonal distortion do not differ much, and in fact are both representative of good metallic behavior, showing that the MIT cannot be related purely to $\Delta_{t_{2g}}$. Notice that at the local level, external pressure decreases $\Delta_{t_{2g}}$, resulting in a sudden increase in $n_{a_{1g}}$ around $\Delta_{t_{2g}} = 0.28$ $eV$ [6]. Turning on the local interactions, $U, J_H$ and $U' = (U - 2J_H)$ will push up most of the spectral weight to the Hubbard sub-bands, and strong $J_H$ will favor $S = 1$ at each $V$ site. So, while these “ground state” features are reasonably well accounted for by LDA($+U$), aspects like the mixed orbital configuration, the switch in orbital occupation at the MIT accompanied by dynamical SWT require a reliable treatment of dynamics of correlated electrons.

Thus, the one-particle part (LDA) of the Hamiltonian is

$$H_0 = \sum_{k\alpha\beta} \epsilon_{\alpha\beta}(k)c_{k\alpha\beta}^\dagger c_{k\alpha\beta}$$

with the total DOS, $n^{0\text{total}}(\epsilon) = \sum_{k\alpha\beta} \delta(\epsilon - \epsilon_{\alpha\beta}(k))$, and $\alpha, \beta = a_{1g}, e_g^\pi, e_g^\sigma_2$. To avoid double counting of interactions which are already treated on the average by LDA, we follow [13] to write

$$H^{0\text{LDA}}_{\text{LDA}} = \sum_{k\alpha\beta} \epsilon_{\alpha\beta}(k)c_{k\alpha\beta}^\dagger c_{k\alpha\beta} + \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}n_{i\alpha\sigma},$$

where $\epsilon_{i\alpha\sigma} = \epsilon_{i\alpha\sigma} - U(n_{\alpha\sigma} - \frac{1}{2}) + \frac{1}{2}J_H(n_{\alpha\sigma} - 1)$, with $U, J_H$ as defined below.

With the interactions in the $t_{2g}$ sector, the full Hamiltonian reads

$$H = H_0 + U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \sum_{\alpha\beta\sigma\sigma'} U_{\alpha\beta}^{\sigma\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'}.$$

Constrained LDA calculations yield $U = 5 - 6$ $eV$ (without inclusion of screening of $t_{2g}$ interactions by $e_g$ electrons), $J_H \approx 1$ $eV$, and $U_{\alpha\beta}^{\sigma\sigma'} \equiv U' = (U - 2J_H) = 3 - 4$ $eV$. Following [13], we use the fact that the $e_g^\sigma$ bands are well separated from the $t_{2g}$ bands to consider only the $t_{2g}$ manifold. Furthermore, in the PM and para- orbital phase, we have $G^{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta}\delta_{\sigma\sigma'}G^{\alpha\sigma}(\omega)$ and $\Sigma^{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta}\delta_{\sigma\sigma'}\Sigma^{\alpha\sigma}(\omega)$.

In the $t_{2g}$ sub-basis, a DMFT solution involves (i) replacing the lattice model by a self-consistently embedded multi-orbital, asymmetric Anderson impurity model, and (ii) a selfconsistency condition which requires the impurity propagator to be equal to the local ($k$-averaged) Green function of the lattice, given by

$$G^{\alpha}(\omega) = \frac{1}{V_B} \int d^3 k \left[ \frac{1}{(\omega + \mu)1 - H^{LSDA}_{\text{LSDA}}(k) - \Sigma(\omega)} \right]_\alpha.$$

Using the locality of $\Sigma^{\alpha\beta}$ in $d = \infty$, we have $G^{\alpha}(\omega) = G^{\alpha}\Sigma^{\alpha}(\omega)$ from the Hilbert transform of the LDA DOS. Also, importantly, the inter-orbital couplings scatter electrons between the $a_{1g}, e_g^\pi$ bands, so that only the total number, $n_{t_{2g}} = \sum_{\alpha} n_{t_{2g}\alpha}$ is conserved in a way consistent with Luttinger’s theorem.

To solve the multi-orbital, asymmetric Anderson impurity problem, we use the iterated perturbation theory (IPT), suitably generalized to the case of $t_{2g}$ orbitals for arbitrary filling [13]. The local propagators are given by

$$G^{\alpha}(\omega) = \frac{1}{N} \sum_k \frac{1}{\omega - \Sigma^{\alpha}(\omega) - \epsilon_{\alpha \bar{k}}},$$

Local self-energies $\Sigma^{\alpha}(\omega)$ are computed within an extended IPT scheme that explicitly satisfies the generalized Friedel sum rule (Luttinger’s theorem) to a very good accuracy. Mathematically,

$$\Sigma^{(2)}(\omega) = \frac{\sum_\gamma A^{\gamma}\Sigma^{(2)}(\omega)}{1 - \sum_\gamma B^{\gamma}\Sigma^{(2)}(\omega)}$$

where, for example,

$$\Sigma^{(2)}(\omega) = N_\alpha \frac{U^2}{\beta^2} \sum_{n,m} G^{\alpha}_n(i\omega_n)G^{\alpha}_m(i\omega_m)G^{\alpha}_n(i\omega_n + i\omega_m - i\omega)$$

with $N_\alpha = 2$ for $\alpha, \gamma = e_g^\pi, e_g^\sigma_2$ and 4 for $\alpha, \gamma = a_{1g}, e_g^\pi, e_g^\sigma_2, e_g^\sigma_2$. The bath propagator is $G^{\alpha}_0(\omega) = [\omega + \mu_{\alpha} -$
$\Delta_\alpha(\omega)^{-1}$. In the above, $A_{\alpha\gamma} = \frac{n_\alpha(1-2n_\alpha)+D_{\alpha\gamma}[n]}{n_0^4(1-n_0^4)}$ and $B_{\alpha\gamma} = \frac{1}{4} \frac{1}{n_0^2(1-n_0^2)}$. Also, $n_\alpha$ and $n_0^\alpha$ are particle numbers defined from $G_\alpha$ and $G_0^\alpha$, and the inter-orbital correlation function is $D_{\alpha\gamma}[n] = \langle n_\alpha n_\gamma \rangle = \langle n_\alpha \rangle \langle n_\gamma \rangle - \frac{1}{2} \int_{-\infty}^{\infty} f(\omega) \text{Im}[\Sigma_\alpha(\omega)G_\alpha(\omega)]d\omega$. This last identity follows directly from the equation of motion for $G_\alpha(\omega)$.

These coupled equations are solved self-consistently to obtain the spectral function. We choose $\Delta_{trg} \simeq 0.32$ eV, completely consistent with the LDA. To study the MIT, we notice that external pressure decreases the quantity $\Delta_{trg} = E_{a_{1g}} - E_{g^\pi}$ and leads to an increase in $n_{a_{1g}}$; in particular, it leads to a reduction in $\Delta_{trg}$ across 0.28, at which point, a sudden increase in $n_{a_{1g}}$ has been reported from cluster calculations [6]. To study this effect, we monitor the spectral function for different values of $n_{a_{1g}}$, with fixed total number of electrons.

In Fig. 3, we show the partial DOS for the $e_{g}^{\pi}$, $a_{1g}$ orbitals, for the metallic (dashed) and “Mott” insulating (solid) phases, corresponding to total $a_{1g}$ occupation $n_{a_{1g}} = 0.41$, 0.36, respectively. As expected from the trigonal splitting assignment, the lower-lying $e_{g}^{\pi}$ orbitals are more localized in the solid, with a gap, $\Delta_{e_{g}^{\pi}} = 0.45$ eV. Correspondingly, the $a_{1g}$ band is more itinerant, completely consistent with the fact that $t_{a_{1g},a_{1g}}$ is by far the largest hopping integral in the real system. From Fig. 2, we estimate $\Delta_{trg} = 0.35$ eV. With $n_{a_{1g}} = 0.41$, the $e_{g}^{\pi}$ spectral function still exhibits insulator-like features, while the $a_{1g}$ spectrum develops a very narrow, quasi-coherent peak with a FWHM = 0.07 eV at $E_F$. We interpret these results as a microscopic derivation of the phenomenological “two-fluid” models proposed earlier to understand metal-insulator transitions [3]. In our new picture, increasing pressure decreases $\Delta_{trg}$, resulting in increased population of the $a_{1g}$ orbital, and leading (via $t_{a_{1g},a_{1g}}$) to an abrupt MIT accompanied by large dynamical SWT.

Using the corresponding self-energy, we carry out a quantitative estimate for the effective mass enhancement and the $A$-coefficient of the low-$T$ quadratic term in the $dc$ resistivity. Indeed, from $Re[\Sigma_{a_{1g}}(\omega)]$, we estimate $m^*/m = \left[1 - \frac{\partial^2 \Sigma_{a_{1g}}(\omega)}{\partial \omega^2}\right]^{-1} = 4.16$, close to the value of 4.4 extracted from low-$T$ specific heat measurements. Also, $A = \rho_{dc}(T)/T^2 = (m^*/ne^2)[\partial^2 \Sigma_{a_{1g}}(\omega)/\partial \omega^2]$ is large, because $\partial^2 \Sigma_{a_{1g}}(\omega)/\partial \omega^2 = 38 \gg 1$. This will result in a large quadratic term in the low-$T$ $dc$ resistivity, as observed.

In Fig. 3, we show the integrated PES and IPES spectra in the metallic and insulating phases, along with the corresponding LDA spectra. As one would expect, and consistent with observations, the PES spectrum shows a very narrow quasi-coherent peak, with most of the spectral weight in the incoherent “lower Hubbard band”, centered at $\omega = -3.0$ eV. The PES intensity at $E_F$ is strongly reduced from the LDA prediction. Quantitative comparison with the PES spectra measured at higher $T$ needs an extension of our approach to finite $T$; however, we expect that the strong $T$-dependence of the quasi-coherent feature within DMFT will smear out the low-energy peak for $T > T_{coh} \simeq 300$ K, bringing the spectra in closer agreement with published PES results. Signatures of strong correlations are also visible in the IPES spectra as “upper Hubbard band” features, and the difference between the LDA and LDA+DMFT spectra is striking.

Especially interesting is the change in the spectral function at $E_F$ as a function of $n_{a_{1g}}$. In Fig. 4, we show this variation for our chosen parameter set. Astonishingly, $\rho(E_F)$ exhibits a sharp jump from 0 to 0.261...
and find that both decrease across the MIT. Further, we find those estimated by polarized XAS measurements [5], but calculated orbital occupations are slightly different from D. We have not attempted to make a detailed comparison with finite-T > 170 K spectral functions in the PI and PM regions, a program which has been carried out in Ref. [3] (but only for T > 400 K, where the first-order MIT is replaced by a smooth crossover), and we plan to report these aspects, along with finite-T transport properties and lattice effects, in a future work.

In conclusion, we have presented a different scenario, based on combination of LDA bandstructure with dynamical, local spin and orbital correlations, to understand salient features of the first-order MIT in the P-phase of V$_2$O$_3$. The first-order MIT is shown to be accompanied by changes in orbital occupation in a way qualitatively consistent with observations. Further, very good agreement with low-T thermodynamic and dc resistivity is obtained within the same approach. This represents a new picture for the correlation-driven MIT in V$_2$O$_3$; one which has applications to other systems where coupled spin-orbital correlations result in changes in orbital occupations across the MIT. Such an approach should be applicable, with extensions to include broken symmetries in the spin/orbital sectors, to systems like Cu$_2$-xSr$_x$RuO$_4$ as well.

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